

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

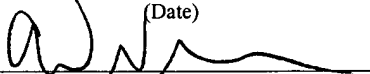
**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



AF PATENT 1765  
Case Docket No. SEPP9.001APC  
Date: July 2, 2004  
Page 1

In re application of : Leskela et al.  
Appl. No. : 09/787,062  
Filed : June 28, 2001  
For : METHOD FOR GROWING  
OXIDE THIN FILMS  
CONTAINING BARIUM  
AND STRONTIUM  
Examiner : Matthew A. Anderson  
Art Unit : 1765

I hereby certify that this correspondence and all marked attachments are being deposited with the United States Postal Service as first-class mail in an envelope addressed to: Mail Stop Appeal Brief - Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on

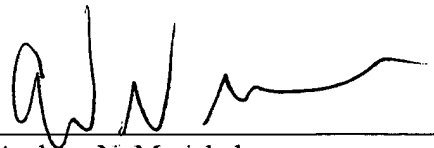
July 2, 2004  
(Date)  
  
Andrew N. Merickel, Reg. No. 53,317

**Mail Stop Appeal Brief - Patents**  
**Commissioner for Patents**  
**P.O. Box 1450**  
**Alexandria, VA 22313-1450**

Sir:

Transmitted herewith in triplicate is an Appellants' Brief to the Board of Patent Appeals:

- (X) Fee for filing brief in the amount of \$330 is enclosed.
- (X) A check in the amount of \$330 to cover the foregoing fees is enclosed.
- (X) If applicant has not requested a sufficient extension of time and/or has not paid any other fee in a sufficient amount to prevent the abandonment of this application, please consider this as a Request for an Extension for the required time period and/or authorization to charge our Deposit Account No. 11-1410 for any fee which may be due. Please credit any overpayment to Deposit Account No. 11-1410.
- (X) Return prepaid postcard.

  
Andrew N. Merickel  
Registration No. 53,317  
Attorney of Record  
Customer No. 20,995  
(415) 954-4114

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## BEFORE THE TRADEMARK TRIAL AND APPEAL BOARD



Applicant : Leskela et al.  
 Appl. No. : 09/787,062  
 Filed : June 28, 2001  
 For : METHOD FOR GROWING  
 OXIDE THIN FILMS  
 CONTAINING BARIUM AND  
 STRONTIUM  
 Examiner : Matthew A. Anderson  
 Group Art Unit : 1765

## CERTIFICATE OF MAILING

I hereby certify that this correspondence and all marked attachments are being deposited with the United States Postal Service as first-class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on

July 2, 2004

(Date)

Andrew N. Merickel, Reg. No. 53,317

**ON APPEAL TO THE BOARD OF PATENT APPEALS AND INTERFERENCES**  
**APPELLANT'S BRIEF**

Dear Sir:

This Appeal Brief relates to an appeal to the Board of Patent Appeals and Interferences of the Final Rejection set forth in an Office Action mailed on January 30, 2004 in the above-captioned application.

**I. REAL PARTY IN INTEREST**

The real party in interest in this appeal is the assignee of this application, ASM International N.V.

**II. RELATED APPEALS AND INTERFERENCES**

Appellants are unaware of any related appeals or interferences.

07/09/2004 AWONDAF1 00000073 09787062

01 FC:1402

330.00 DP

**III. STATUS OF THE CLAIMS**

The present application was originally filed with Claims 1-19. Claims 1-19 were amended and Claims 20-27 were added in a preliminary amendment filed March 12, 2001.

**Appl. No.** : **09/787,062**  
**Filed** : **June 28, 2001**

Claims 28-35 were added in the Amendment and Response to Office Action filed on December 13, 2002. Claims 36-39 were added with the Request for Continued Examination filed on May 29, 2003. Claims 1-39 are thus pending in the present application and have been finally rejected in the Office Action dated January 30, 2004. This final rejection was affirmed in the Advisory Action mailed on April 15, 2004.

Accordingly, Claims 1-39 are the subject of this appeal. These claims are attached hereto as Appendix A.

#### **IV. STATUS OF AMENDMENTS**

The claims before the Board appear as they were finally rejected. These pending claims are attached hereto as Appendix A.

#### **V. SUMMARY OF THE INVENTION**

The present invention relates to the deposition of thin films with high dielectric constants by atomic layer deposition (ALD). In particular, methods of depositing thin films comprising barium and/or strontium are disclosed. Oxide thin films containing barium and strontium are dielectric films with high permittivities that are widely used and have been well studied. While these films have been manufactured by many different methods, including sol-gel methods, physical vapor deposition (PVD) methods and chemical vapor deposition (CVD) methods, each of these methods has known problems. As a result, it has not been possible to deposit highly conformal high-quality thin films on a substrate with a complicated three dimensional structure. Even using the CVD method, high conformality is attained only when the rate of film growth is determined by the rate of the surface reaction and not by the diffusion of the precursors on the film surface. This is achieved when the surface reaction is slower than the diffusion of the precursors on the film surface, which occurs only at low temperatures. However, at low temperatures, the film has poor crystallinity and it is difficult to control the composition of the film (page 2, lines 9-22 of the Specification).

The present invention overcomes the disadvantages in the prior art methods by using atomic layer epitaxy (ALE) to deposit high-K dielectric layers comprising barium and/or strontium with almost perfect conformality, unlike those deposited by CVD. The ALE methods are facilitated by the use of particular barium and/or strontium precursors.

**Appl. No.** : **09/787,062**  
**Filed** : **June 28, 2001**

The appealed claims reflect the disclosed invention. Claim 1, for example, recites a method for growing oxide thin films on a substrate in a reactor comprising producing the films by an ALE process. The ALE process comprises feeding pulses of precursor compounds into the reactor alternately to achieve film growth through saturating, self-limiting surface reactions. The reactor is purged with an inert gas between the precursor pulses. The precursor compounds comprise at least one cyclopentadienyl compound of strontium and/or barium, at least one volatile titanium compound and a reactive oxygen precursor. Independent Claims 27, 28, and 36 similarly recite a method for growing oxide thin films on a substrate by self-limiting atomic layer epitaxy utilizing cyclopentadienyl precursor compounds.

## **VI. ISSUES BEFORE THE BOARD**

This appeal turns on whether Claims 1-39 are properly rejected under 35 U.S.C. § 103(a) as being unpatentable over DiMeo (U.S. Patent No. 5,972,430) in view of Kirlin (U.S. Patent No. 5,453,494) and/or Maiti (U.S. Patent No. 6,020,024).

## **VII. GROUPING OF CLAIMS**

For the purposes of the present appeal, Claims 1-39 stand and fall together. Appellants reserve the right, however, to separately argue in subsequent continuing applications the patentability of various features not addressed herein.

## **VIII. APPELLANT'S ARGUMENT**

In the Final Office Action mailed on January 30, 2004, the Examiner rejected Claims 1-39 under 35 U.S.C. § 103(a) as being unpatentable over DiMeo, Jr. et al. (U.S. Patent No. 5,972,430) in view of Kirlin et al. (U.S. Patent No. 5,453,494) and Maiti et al. (U.S. Patent No. 6,020,024). According to the Examiner, DiMeo discloses a CVD method for forming multi-component oxide layers. The Examiner asserts that the CVD method is an "equivalent variant" to atomic layer epitaxy (ALE). Kirlin et al. is found to disclose barium and strontium precursors including cyclopentadienyl compounds for use in metal organic CVD (MOCVD). Maiti et al. is found to disclose the annealing of metal oxides in order to fully oxidize a metal oxide dielectric layer. The Examiner concludes that it would have been obvious to one of ordinary skill in the art to combine the prior art references to produce the claimed invention. However, Claims 1-39 are

**Appl. No.** : 09/787,062  
**Filed** : June 28, 2001

not obvious because the prior art does not teach all of the elements of the claims, provides no motivation or suggestion for modifying and combining the references in the claimed manner, and provides no expectation of success in the claimed combinations.

**A. Factual Errors**

Applicants note that the Examiner's rejections rest on two factual errors:

1. **First factual error:** The Examiner states that "The CVD method [of DiMeo] is described as an *equivalent variant* to the related ALE (atomic layer epitaxy)." Office Action mailed on January 30, 2004 at p. 2 (*emphasis added*). This statement is simply not true. Nowhere does DiMeo state that CVD and ALE are equivalent variants. Instead, DiMeo states that "[o]f the method for forming multi-component oxide thin film layers, chemical vapor deposition (CVD) methods and *related* epitaxial deposition methods, such as but not limited to atomic layer epitaxial (ALE) deposition methods, are in turn also *presently of interest*." DiMeo, Col. 1, ll. 44-50 (*emphasis added*). It is nonsensical to conclude that a process taught as "related" to CVD and "presently of interest" is, therefore, necessarily an equivalent variant. To the contrary, the fact that DiMeo clearly makes a distinction between CVD and ALE in the Background section is more properly construed as evidence that they are distinct processes, rather than equivalent variants. For instance, immediately after mentioning ALE and CVD, DiMeo implies that ALE and CVD are, in fact, variants (not equivalent variants) by referring to "*[a]dditional variants* upon chemical vapor deposition (CVD) methods and epitaxial deposition methods...." DiMeo, Col. 1, ll. 50-52 (*emphasis added*). The substantial distinctions between ALE and CVD are discussed in detail below.
2. **Second factual error:** "The examiner notes that the version of claims added 11/17/2003 *does not require saturating surface reactions*." Office Action at p. 7 (*emphasis added*). This statement is also false. Every independent claim recites "saturating surface reactions" (Claims 1, 27, and 28) or "saturating...surface reactions" (Claim 36). It follows that the Examiner's rejections are based upon an erroneous reading of Applicants' claims. As a result of failing to ascertain all the

Appl. No. : 09/787,062  
Filed : June 28, 2001

elements of Applicants' claims, the Examiner has not provided a combination of references teaching each and every element of Applicants' claims.

**B. The Cited Art Neither Teaches Nor Suggests All The Elements Of The Claimed Combination**

The Examiner bears the initial burden to establish and support *prima facie* obviousness. See *In re Rinehart*, 531 F.2d 1048, 189 U.S.P.Q. 143 (C.C.P.A. 1976). In order to establish a *prima facie* case of obviousness, **each** of the elements of a claim must be taught or suggested in the prior art. M.P.E.P. § 2143.03, citing *In re Royka*, 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974). Further, "**all** words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 424 F.2d 1382, 1385, 165 U.S.P.Q. 494, 496 (C.C.P.A. 1970). Here, the prior art relied on by the Examiner **does not** teach or suggest each of the elements of the claims.

Applicants submit that the Examiner has not shown any teaching to suggest employing the recited precursor in a manner that meets Applicants' recitation of "ALE," "saturating surface reactions" or "self-limiting." Applicants recite in every claim an "atomic layer epitaxy (ALE)" process including "saturating surface reactions" (Or "saturating ... surface reactions") using a cyclopentadienyl precursor or compound. In addition, every claim recites that the ALE process is "self-limiting."

The Federal Circuit has mandated that, "[i]n construing a claim, claim terms are given their **ordinary and accustomed meaning** unless examination of the specification, prosecution history, and other claims indicates that the inventor intended otherwise." *Nike Inc. v. Wolverine World Wide, Inc.*, 33 U.S.P.Q. 2d 1038, 1039 (1994) (*emphasis added*). In addition, "although the PTO must give claims their broadest **reasonable interpretation**, this interpretation **must be consistent with the one that those skilled in the art would reach**." *In re Cortright*, 49 U.S.P.Q. 2d 1458, 1467 (Fed. Cir. 1999) (*emphasis added*). See also *In re Morris*, 44 U.S.P.Q. 2d 1023, 1027 (Fed. Cir. 1997). Furthermore, the M.P.E.P. clearly states that "the words of a claim...must be read as they would be interpreted by those of ordinary skill in the art." §2111.01.

It follows from the above that the Examiner must consider the "ordinary and accustomed meaning" unless Applicants have indicated an intention to deviate from this meaning. In the present case, Applicants have not indicated any intention to deviate from the ordinary and

Appl. No. : 09/787,062  
Filed : June 28, 2001

accustomed meaning of the terms "Atomic Layer Epitaxy (ALE)," "self-limiting," and "saturating surface reactions;" on the contrary, Applicants have repeatedly emphasized the ordinary and accustomed meaning of the terms at issue. As a result, these recited terms must be given "their broadest reasonable interpretation....consistent with the one that the those skilled in the art would reach."

None of the references cited by the Examiner provide any teaching or suggestion of an ALE process comprising saturating, self-limiting surface reactions and utilizing a cyclopentadienyl precursor or compound. Rather, each of the three asserted references is a **chemical vapor deposition (CVD)** reference in which the disclosed deposition methods **do not** comprise saturating surface reactions and are not self limiting. As is known in the art, CVD methods will continue to deposit as long as reactants are available, contrary to the meaning of "ALE" and "self-limiting" and "saturating surface reactions" as the skilled artisan would understand those terms. Thus, Applicants assert that the Examiner has failed to provide references that teach each and every element of Applicants' claims. As a result, the Examiner has not established a *prima facie* case of obviousness.

ALE (otherwise known as ALD) is a term of art for a deposition process that differs from CVD. The skilled artisan would understand that ALE, unlike CVD, involves depositing a layer upon a substrate through alternating, self-limited saturating surface reactions, as recited in the pending claims. The enclosed Bedair article (Bedair, S.M., Journal of Vacuum Science Technology B, 12 (1), pp. 179-185, 179 (Jan/Feb 1994); attached hereto as Appendix E) provides evidence of the skilled artisans understanding of ALE as compared to CVD, as reflected in the following passage:

In **contrast** to MBE [molecular beam epitaxy] and **MOCVD** [metal organic chemical vapor deposition] growth, in which reacting precursors are introduced **simultaneously** and reach the substrate surface together, ALE growth of III-V compounds, for example, proceeds by exposing the substrate surfaces to group III precursors in the **absence** of group V precursors, followed by exposing the substrate surface of group V precursors in the **absence** of group III precursors. Accordingly, the **basic principle of ALE growth** is based on **alternating** chemisorption, surface reaction, and desorption of the reactants. ALE growth is characterized by its **self-limiting** deposition process...[and] ALE growth promises extremely uniform thickness and very good growth reproducibility...[, t]hese are **difficult to achieve by conventional growth methods** where all the reacting species are **mixed together** on top of the substrate." (*Emphasis Added*).



ALE deposition is inherently self-limited in that, once the substrate surface is saturated with a given reactant, deposition effectively ends and no more of that reactant will adsorb *regardless of the amount* of that reactant flowed across the substrate. As a result, all that is required to deposit an atomic layer of a reactant is to ensure precursor is injected at or greater than the amount needed to saturate the substrate surface, *i.e.*, overshooting the saturation point does not affect the deposition thickness. In other words, ALE automatically effectuates a highly precise deposition without necessitating precise mechanical control over reactant supplies. In contrast, the thickness of a layer deposited by CVD is *not self-limiting* (even if it results in one atomic layer being deposited), but rather is *always supply dependent*, *i.e.*, thickness is controlled via injection and/or pulse duration and a thick layer can be deposited in bulk with a single pulse.

Here, in the absence of an ALE reference the Examiner has maintained that DiMeo's pulse limited CVD or digital CVD process is "an equivalent variant" of ALE. This is not the case. The distinctions between ALE and CVD pointed out generally above are applicable to the present situation. Thus, one important distinction between DiMeo's CVD processes and Applicants' claimed ALE method is that the growth rate by ALE is necessarily self-limited, while the growth rate by CVD can be manipulated by modifying the source chemical dosage. In particular, while the growth rate using CVD can vary across a wide range depending on the source chemical dosage, the growth rate for an ALE process is *self-limited* to one monolayer or less per cycle by the *self-saturating surface reactions*. Accordingly, ALE is not sensitive to the dosage of the source chemical, while CVD requires that the source chemical dosage be precisely controlled.

An example of the need for precise control of the source chemical dosage in CVD is explicitly taught in DiMeo; "Typically and preferably, the multi-component oxide precursor layer is formed over the substrate 14 to a thickness of from about 5 to about 100 Angstroms *employing an appropriate precursor reactant source materials flow rate.*" Col. 9, lines 34-38 (*emphasis added*). Thus, according to the process disclosed in DiMeo the thickness of the multi-component oxide precursor layer correlates with the precursor reactant source materials flow rate. Contrary to this, in the claimed ALE processes the growth rate is not sensitive to the reactant flow rate because each deposition cycle adds no more than one molecular monolayer of metal oxide to the film thickness through *saturating surface reactions*. Although a skilled artisan would understand these qualities to be inherent to an ALE process, Applicants clarified this distinction

during prosecution by amending the independent claims to recite “achieve[ing] film growth through saturating surface reactions” (Claims 1, 27, and 28) and employing “saturating, self-limiting surface reactions on the substrate” (Claim 36).

Contrary to the ordinary and customary meaning of “ALE”, “self-limiting” and “saturating surface reactions,” the Examiner maintains that the cited references, in combination, teach a self-limited ALE process based on his conclusion that the “combination of references...discloses *purging* between growth steps in an atomic layer CVD deposition process indicating to the ordinary skill artisan a limited process.” Office Action at p. 6 (*emphasis added*). In explaining his position, the Examiner states the following:

“The examiner is not persuaded by the argument that the ALE process is self limited while that of DiMeo is not. The applicant ignores the purging of excess precursor in DiMeo et al. One of ordinary skill would conclude that *this purging limits the precursor available* in the deposition chamber for the oxidation reaction.”

Office Action at p. 8 (*emphasis added*).

However, the Examiner’s logic, as evidenced by the passage quoted above, only supports the conclusion that DiMeo’s process is *limited* (not self-limited) through *external control*, i.e. a computer controlling reactive pulse length and inert purge timing to control deposition. This does not mean that the reactions of DiMeo are *self-limiting*. In a CVD reaction, the reactants themselves do not inherently, by their chemistry, limit deposition thickness. It is the external, mechanical control of the valves that limits the reaction, thereby limiting film thickness. Thus, while the CVD process of DiMeo may be limiting, as the Examiner asserts, it is not *self-limiting*.

The skilled artisan would *not* consider the term “self-limiting” in an “ALE process” to encompass a purge-limited deposition process. To the contrary, the skilled artisan understands that an ALE process is limited by the number of available binding sites and not by the amount of precursors. That is, the skilled artisan understands that ALE processes are *self-limited* by virtue of “saturating surface reactions,” rather than limited by factors external to the reaction, such as reactive pulse length or purge timing, as taught in DiMeo.

Further, in contrast to the monolayer by monolayer growth of an ALE reaction, DiMeo teaches deposition of multiple molecular layers in each cycle. This is evidenced by the statement that “[t]he barium strontium titanate (BST) layers were formed upon the first series of substrates employing the foregoing conditions for a total of 100 cycles, which provided barium strontium titanate (BST) layers of total thicknesses [of] about 3300 Angstroms.” Col 12, ll. 53-57.

Accordingly, DiMeo teaches a method yielding a BST growth rate of 33 Å/cycle (3300 Angstroms per 100 cycles). The thickness of one molecular monolayer of a metal oxide is close to the lattice constant of the metal oxide. For example, the lattice constant of cubic BaO is 4.0 Å and the lattice constants of tetragonal SrO are 3.7 and 4.0 Å (R. Kita et al., J. Mater. Res. 8 (1996) p. 321, copy enclosed). Thus, several molecular monolayers were formed during each cycle on the substrate in DiMeo's process.

In comparison, multiple molecular monolayers are *not* formed in an ALE process. Rather, in ALE processes the substrate surface is saturated with *no more than one molecular monolayer* of the precursor. What is important is that in an ALE process the thickness of the deposited layer depends on, and is limited by, the saturating surface reaction, which in turn depends on the nature of the source chemicals. In other words, ALE layers can not be deposit more than one molecular layer at a time because in each reaction cycle when all binding sites for precursor molecules are full, no more precursor is able to bind. In fact, the growth rate in ALE processes is typically less than one molecular monolayer per cycle because of steric interactions between bulky source chemical molecules (large ligands, e.g. cyclopentadienyl ligands). Again, Applicants have amended the claims to clearly recite saturating surface reactions. In comparison, CVD processes, such as DiMeo's, are *not* limited by saturating surface reactions. Importantly, because of the differences in the growth mechanism, as evidenced by the different growth rates, the requirements for the source chemicals in ALE and CVD are necessarily different and compounds that are useful in CVD reactions are not necessarily useful in ALE processes.

In view of the above, it is clear that the CVD method of the primary reference, DiMeo, is fundamentally different from atomic layer epitaxy (ALE) methods with respect to both the means employed and ends achieved. The skilled artisan would recognize the fundamental differences and realize that these disparate methods are not automatically combinable or interchangeable, without particular suggestions.

As evidence of the skilled artisan's understanding of an ALE process and to highlight the distinctions between ALE and CVD, Applicants submitted two references (Vehkamäki et al. Electrochemical and Solid-State Letters, 2, pp. 504-506 (1999); and M. Nakano et al. Appl. Phys. Lett., 57, pp. 1096-1098 (1990), attached as Appendix F). In the final Office Action mailed on January 30, 2004, the Examiner refused to consider these references because they were not made of record. However, these references were not submitted as prior art references, but rather to

Appl. No. : 09/787,062  
Filed : June 28, 2001

inform the Examiner as to the ordinary and customary meaning of Applicants' claim language to the skilled artisan. Accordingly, Applicants were under no obligation to submit these references on a PTO Form 1449. However, in order to address the Examiner's concern, Applicants included a 1449 citing these three references with their Request for Reconsideration submitted on April 2, 2004. The Examiner maintained his refusal to consider these references in the Advisory Action mailed on April 15, 2004, thus *refusing to consider evidence* of non-obviousness submitted prior to the final rejections.

In Vehkamäki et al., the growth rate of  $\text{SrTiO}_3$  by ALE was shown to be  $0.7 - 1.8 \text{ \AA/cycle}$  depending on the Sr/Ti cycle ratio, while the growth rate of  $\text{BaTiO}_3$  was  $0.5 \text{ \AA/cycle}$ . These measurements are equivalent to one monolayer of the compound per cycle and are representative of an ALE process.

In comparison, the teachings in Nakano of a CVD method are representative of the inherent qualities of CVD. In the abstract, Nakano teaches that "[t]he repetitive cycles of a few monolayers hydrogenated silicon deposition and its oxidation has been employed for the growth of  $\text{SiO}_2$ ." The growth rate of a few monolayers per cycle means that digital chemical vapor deposition is *not* based on self-saturating surface reactions.

Nakano also teaches that "[a]t the present stage,  $\text{SiO}_2$  could not be filled in trenches with aspect ratios larger than 3." Nakano at p. 1097. This indicates that chemical vapor deposition is not capable of growing film in relatively deep trenches. In comparison, ALE can advantageously grow thin films in deep trenches or similarly high stepped topography because the alternate, self-saturating surface reactions produce conformal films.

Another inherent property of CVD is illustrated by Nakano's teaching that "[t]he deposition rate of  $3 \text{ \AA/pulse}$  is achieved by controlling the flow velocity of the  $\text{SiH}_4$  gas jet and the pulse width of the  $\text{O}_2$  radicals." Nakano at p. 1098. Thus, Nakano confirms DiMeo's teaching that deposition rate in CVD depends on precursor flow rate.

In view of Nakano's teachings, it is clear that chemical vapor deposition processes (e.g., the CVD process of DiMeo) have different requirements than ALE processes. Chemical vapor deposition requires controlling the dosage of the source chemicals in order to achieve a thin film of the desired thickness. Contrary to this, ALE processes are not sensitive to the dosage of the source chemical because of the self-saturating nature of the surface reactions. One of skill in the

Appl. No. : 09/787,062  
Filed : June 28, 2001

art will recognize that these different requirements will necessarily mean that not all source chemicals employed for CVD will be suited for ALE processes.

In contrast to the evidence provided by Applicants, the Examiner has only offered conclusory statements that DiMeo's purge limited process teaches a self-limiting process using saturating surface reactions as claimed. The Examiner's conclusions are based upon absolutely no evidence showing that the skilled artisan would interpret Applicants' claims in a way consistent with the Examiner's interpretation. It follows that it is *unreasonable* for the Examiner to continue to interpret "self-limiting" to be met by the purge-limited process of DiMeo when the ordinary and customary meaning of self-limiting is clearly not broad enough to include such a processes. *In re Cortright*, 49 U.S.P.Q. 2d 1458, 1467 (Fed. Cir. 1999). When Applicants' claims are interpreted using the "broadest *reasonable* interpretation," the cited references fail to teach or suggest each and every element of Applicants' claims. *Cortright* at 1467.

**C. The Prior Art Provides No Motivation Or Suggestion To Make The Claimed Combination**

Even if the references cited by the Examiner disclose all the features of the presently claimed invention, the references would not create a *prima facie* showing of obviousness. This is because obviousness can only be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either explicitly or implicitly in the references themselves or in the knowledge generally available to one of ordinary skill in the art. M.P.E.P. § 2143.01, citing *In re Kotzab*, 217 F.3d 1365, 1370, 55 U.S.P.Q.2d 1313, 1317 (Fed. Cir. 2000).

Thus, the Examiner must show an expectation of success for and the desirability of employing in an ALE process the particular compounds that have been identified as CVD precursors. The Examiner has shown neither functionality nor desirability. That is, the Examiner has provided no evidence in DiMeo or elsewhere that the particular precursors would work in an ALE process, or that one of skill in the art would be motivated to use the precursors in an ALE process. As a result, the Examiner has not provided the requisite teaching or suggestion to combine the passing reference to ALE in DiMeo's background with the CVD precursors described in DiMeo's detailed description (i.e., incorporated from Kirlin).

**Appl. No.** : **09/787,062**  
**Filed** : **June 28, 2001**

The Examiner's assertion that precursors that work in CVD will also work in ALE is clearly erroneous and without support. As discussed above and evidenced by the references provided herewith, ALE is not a subset or equivalent of CVD. To the contrary, ALE and CVD employ different mechanisms and thus have different requirements. For example, precursors used in ALE must be able to provide saturating, self-limiting surface reactions. CVD precursors do not need to have this ability. Because of their different requirements, not all CVD precursors will work in an ALE method, to say nothing of their relative desirability in ALE. With respect to the present application, the characteristics of an ALE mechanism which distinguish it from a CVD mechanism are positively recited in the claims.

Even if it were obvious to try the CVD precursors in an ALE reaction, this cannot serve as a basis for rejection under 35 U.S.C. § 103. An "obvious to try" standard has been rejected by the Federal Circuit. *See e.g., In re O'Farrell*, 7 U.S.P.Q.2d 1673 (Fed. Cir. 1998). Instead of merely showing it as obvious to try a combination, the Examiner must show both motivation and an expectation of success by the skilled artisan at the time of the invention. Here, the Examiner has provided no motivation to combine the cited teachings and, as discussed below, has provided no evidence of an expectation of success.

**D. The Prior Art Does Not Provide A Reasonable Expectation Of Success In The Claimed Combination**

In order to establish a prima facie case of obviousness, the Examiner needs to show that the skilled artisan would have expected such a combination to succeed. "Both a suggestion [to combine] and the expectation of success must, be found in the prior art, not in the applicant's disclosure." *In re Dow Chemical Co.*, 5 U.S.P.Q.2d 1529, 1530 (Fed. Cir. 1988). The Examiner cannot merely look to the isolated statements of DiMeo without also determining how these might be interpreted by the skilled artisan and looking to the remainder of the field of interest to determine whether the success of the overall combination is fairly suggested. A single passing reference to ALE in the background section of DiMeo is insufficient, against the entire remaining disclosure (which only teaches a purge-limited CVD process with no mention of ALE or self-limiting, saturating surface reactions), to provide a suggestion to use DiMeo's precursors in an ALE process, much less to provide a reasonable expectation of success. The skilled artisan would understand that CVD and ALE are fundamentally different and, as a result, would

recognize that the distinction between the choice of precursors for CVD processes and the choice of precursors for ALE processes is not trivial. As a result, the skilled artisan will recognize and understand that precursors taught as suitable for CVD are not automatically applicable to ALE, as assumed by the Examiner. Thus, without some teaching or suggestion that the recited precursors will work in an ALE process there would not be a reasonable expectation of success in the claimed combinations.

**E. No Prima Facie Showing of Obviousness Has Been Set Forth**

The prior art cited by the Examiner does not teach or suggest each of the elements of the pending claims as required for a *prima facie* case of obviousness. (M.P.E.P. § 2143.03). Further, there is no motivation to modify the teachings of DiMeo to arrive at Applicants' claimed combinations and no evidence that the skilled artisan would have an expectation of success in utilizing the recited precursors in an ALE process. In the absence of the necessary teachings and motivation in the prior art, the Examiner is improperly relying on Applicants' own disclosure to arrive at a conclusion that the claimed invention is obvious. "The references themselves, not the invention itself, must provide some teaching whereby the Applicant's combination would have been obvious." *In re Gorman*, 933 F.2d 982 (Fed. Cir. 1991); *Heidelberger Druckmaschinen A.G. v. Hantscho Commercial Products, Inc.*, 21 F.3d 1068 (Fed. Cir. 1993). Thus, the current rejection of the claims is in error and Applicants request its withdrawal.

**IX. CONCLUSIONS**

Applicants submit that a skilled artisan would appreciate that ALE is not equivalent to CVD and that DiMeo does not teach or suggest an ALE process utilizing saturating, self-limiting reactions. Further, one of skill in the art would understand that reactants that are suitable for use in CVD processes are not automatically suitable for use in ALE processes. As a result, the skilled artisan reading the DiMeo reference would not have been motivated to use the precursors disclosed therein in an ALE processes. There is simply no motivation or suggestion in DiMeo for the claimed invention. Further, they would have no expectation of success in such use. Hence, because obviousness has not been established, Applicants request that the rejections under 35 U.S.C. § 103 be removed and that Claims 1-39 be allowed.

Appl. No. : 09/787,062  
Filed : June 28, 2001

**X. APPENDIX A**

Attached hereto as Appendix A is a copy of the appealed claims.

**XI. APPENDIX B**

Attached hereto as Appendix B is a copy of DiMeo, Jr. et al. (U.S. Patent No. 5,972,430).

**XII. APPENDIX C**

Attached hereto as Appendix C is a copy of Kirilin et al. (U.S. Patent No. 5,453,494).

**XIII. APPENDIX D**

Attached hereto as Appendix D is a copy of Maiti et al. (U.S. Patent No. 6,020,024).

**XIV. APPENDIX E**

Attached hereto as Appendix E is a copy of Bedair, S.M., Journal of Vacuum Science Technology B, 12 (1), pp. 179-185, 179 (Jan/Feb 1994).

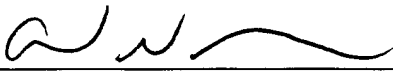
**XV. APPENDIX F**

Attached hereto as Appendix E are the following two references, offered as evidence of Applicants' positions herein: Vehkamäki et al., Electrochemical and Solid State Letters, 2 (10), pp. 504-506 (1999); Nakano et al., Appl. Phys. Lett. 57 (11) pp. 1096-1098 (1990); Bedair, J. Vac. Sci. Technol. B, 12 (1), pp. 179-185 (1994).

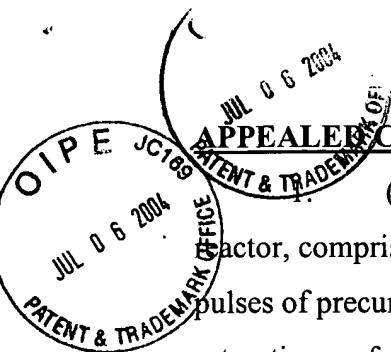
Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: July 2, 2004

By:   
Andrew N. Merickel  
Registration No. 53,317  
Attorney of Record  
Customer No. 20,995  
(415) 954-4114





**APPEALED CLAIMS:**

(Currently Amended) A method for growing oxide thin films on a substrate in a reactor, comprising producing the films by the Atomic Layer Epitaxy (ALE) process by feeding pulses of precursor compounds into the reactor alternately to achieve film growth through saturating surface reactions and by purging the reactor with an inert gas between the precursor pulses to provide alternate self-limiting surface reactions on the substrate, wherein the precursor compounds comprise:

at least one cyclopentadienyl compound of strontium and/or barium;  
at least one volatile titanium compound; and  
a reactive oxygen precursor.

2. (Previously Presented) The method according to Claim 1, wherein the oxide thin film is dielectric.
3. (Previously Presented) The method according to Claim 1, wherein said method comprises 1-10 growth cycles in succession, wherein one growth cycle comprises:  
feeding of a Ba compound, a Sr compound or a volatile titanium compound;  
an inert purge;  
feeding a reactive oxygen precursor; and  
a second inert purge.
4. (Previously Presented) The method according to Claim 1, wherein the ratio of the at least one cyclopentadienyl compound of strontium and/or barium and the at least one volatile titanium compound is 0.8-1.2.
5. (Previously Presented) The method according to Claim 1, wherein the volatile titanium compound is selected from the group consisting of a titanium halide, a titanium alkoxide, titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkyldithiocarbamate, and a titanium- $\beta$ -diketonate.
6. (Previously Presented) The method according to Claim 1, wherein the substrate is selected from the group consisting of a platinum (Pt),  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{SrRuO}_3$ ,  $\text{LaSrCoO}_3$ ,  $\text{IrO}_2/\text{Ir}$ ,  $\text{RuO}_2/\text{Pt}$ , silica ( $\text{SiO}_2$ ), silicon nitride and a silicon surface.
7. (Previously Presented) The method according to Claim 1, wherein the reactive oxygen precursor is selected from the group consisting of oxygen ( $\text{O}_2$ ), water vapor, hydrogen peroxide, an aqueous solution of hydrogen peroxide, ozone, and a combination thereof.

8. (Previously Presented) The method according to Claim 1, wherein the at least one cyclopentadienyl compound of strontium and/or barium is  $M(Cp)_2$  or  $M(Cp)_2L_n$ , where

- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group of the form  $C_5R_mH_{5-m}$ , where
- m is an integer 0-5 and
- R is a hydrocarbon group, wherein the m hydrocarbon groups are either the same or different,
- the Cp groups are either the same or different,
- $L_n$  is a neutral adduct ligand which binds to the metal by one or several of the atoms in said neutral adduct ligand.

9. (Previously Presented) The method according to Claim 1, wherein

- the at least one cyclopentadienyl compound of strontium and/or barium is  $M(Cp)X$  or  $M(Cp)XL_n$ , where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group  $C_5R_mH_{5-m}$ , where
- m is an integer 0-5 and
- R is a hydrocarbon group, wherein the m R's are either the same or different,
- X is a ligand having a valence of -1, wherein X is not a cyclopentadienyl group and
- L is a neutral adduct ligand which binds to the metal by one or several of the atoms making up said neutral adduct ligand.

10. (Previously Presented) The method according to Claim 9, wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, and fluorenyl.

11. (Previously Presented) The method according to Claim 8, wherein the two Cp groups are joined by a bridge.

12. (Previously Presented) The method according to Claim 11, wherein the bridge between the two Cp groups is a substituted or unsubstituted  $C_1 - C_6$  carbon chain.

13. (Previously Presented) The method according to Claim 12, wherein the carbon chain forming the bridge contains a heteroatom selected from the group consisting of silicon, nitrogen, phosphorus, selenium, and sulfur.

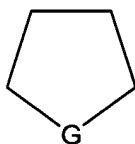
14. (Previously Presented) The method according to Claim 9, wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, an amino, a cyano and a silyl group.

15. (Previously Presented) The method according to Claim 9, wherein the neutral adduct ligand L is selected from the group consisting of:

- (i) a hydrocarbon,
  - (ii) an oxygen-containing hydrocarbon,
  - (iii) a nitrogen-containing hydrocarbon,
  - (iv) a sulfur-containing hydrocarbon,
  - (v) a phosphorus-containing hydrocarbon,
  - (vi) an arsenic-containing hydrocarbon,
  - (vii) a selenium-containing hydrocarbon,
  - (viii) a tellurium-containing hydrocarbon,
- and a combination thereof.

16. (Previously Presented) The method according to Claim 9, wherein L is selected from the group consisting of:

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



, where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano and a silyl group, and wherein each carbon atom of the ring according the formula has an R<sup>1</sup>-like substituent, wherein the substituents are either the same or different,

- (d) ether, and
- (e) thioether.

17. (Previously Presented) The method according to Claim 9, wherein L is selected from the group consisting of an ether, a polyether, an amine, a polyamine, bipyridine and tetrahydrofuran.

18. (Previously Presented) The method according to Claim 9, wherein X is selected from the group consisting of a  $\beta$ -ketonate, a corresponding sulfur or nitrogen compound, an alkyl, a halide, an amide, an alkoxide, a carboxylate and a Schiff base.

19. (Previously Presented) The method according to Claim 1, wherein the producing of the film takes place at 250-300°C.

20. (Original) The method according to Claim 3, wherein said method comprises 1-2 growth cycles.

21. (Original) The method according to Claim 9, wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, and fluorenyl.

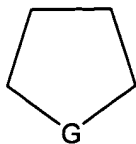
22. (Original) The method according to Claim 9, wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, an amino, a cyano and a silyl group.

23. (Original) The method according to Claim 9, wherein the neutral adduct ligand L is selected from the group consisting of:

- (i) a hydrocarbon,
  - (ii) an oxygen-containing hydrocarbon,
  - (iii) a nitrogen-containing hydrocarbon,
  - (iv) a sulfur-containing hydrocarbon,
  - (v) a phosphorus-containing hydrocarbon,
  - (vi) an arsenic-containing hydrocarbon,
  - (vii) a selenium-containing hydrocarbon,
  - (viii) a tellurium-containing hydrocarbon,
- and a combination thereof.

24. (Original) The method according to Claim 9, wherein L is selected from the group consisting of:

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



, where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano and a silyl group, and wherein each carbon atom of the ring according the formula has an R<sup>1</sup>-like substituent, wherein the substituents are either the same or different,

(d) ether, and

(e) thioether.

25. (Original) The method according to Claim 19, further comprising postannealing said film at a temperature higher than a temperature at which the producing of the film takes place.

26. (Original) The method according to Claim 25, wherein post annealing said film takes place at 500°C.

27. (Currently Amended) A method for growing oxide thin films on a substrate in a reactor, comprising producing the films by the Atomic Layer Epitaxy (ALE) process by feeding alternating pulses of precursor compounds into the reactor alternately to achieve film growth through saturating surface reactions and by purging the reactor with an inert gas between the precursor pulses to provide alternate self-limiting surface reactions on the substrate, wherein the precursor compounds comprise:

at least one cyclopentadienyl compound of strontium and/or barium; and  
a reactive oxygen precursor.

28. (Currently Amended) A method for growing oxide thin films on a substrate in a reactor by self-limiting Atomic Layer Epitaxy (ALE), comprising producing the films by feeding pulses of precursor compounds into the reactor to achieve film growth through saturating surface reactions, wherein a growth cycle comprises:

feeding a first reactant pulse into the reactor, wherein the first reactant is selected from the group consisting of a cyclopentadienyl compound of strontium and a cyclopentadienyl compound of barium;

purging the first reactant from the reactor with an inert gas;  
pulsing a second reactant pulse into the reactor, the second reactant comprising oxygen;  
purging the second reactant from the reactor with an inert gas;  
pulsing a third reactant pulse into the reactor, the third reactant comprising a volatile titanium compound; and  
purging the third reactant from the reactor with an inert gas,  
wherein the second reactant is pulsed between pulses of the first reactant and the third reactant.

29. (Previously Presented) The method of Claim 28, wherein no more than one molecular layer is deposited onto the substrate per growth cycle.

30. (Previously Presented) The method of Claim 28, wherein the first reactant is a cyclopentadienyl compound of strontium.

31. (Previously Presented) The method of Claim 30, wherein the growth cycle further comprises:

pulsing a fourth reactant pulse into the reactor, the fourth reactant comprising a cyclopentadienyl compound of barium; and

purging the fourth reactant from the reactor with an inert gas.

32. (Previously Presented) The method of Claim 30, wherein the growth cycle comprises, in order, pulsing the first reactant, purging the first reactant, pulsing the second reactant, purging the second reactant, pulsing the third reactant and purging the third reactant.

33. (Previously Presented) The method of Claim 30, wherein the growth cycle comprises, in order, pulsing the third reactant, purging the third reactant, pulsing the second reactant, purging the second reactant, pulsing the first reactant, purging the first reactant, pulsing the second reactant and purging the second reactant.

34. (Previously Presented) The method of Claim 28, wherein the first reactant is a cyclopentadienyl compound of barium.

35. (Previously Presented) The method of Claim 34, wherein each cycle further comprises:

pulsing a fourth reactant pulse into the reactor, the fourth reactant comprising a cyclopentadienyl compound of strontium; and

removing the fourth reactant from the reactor with an inert gas.

36. (Currently Amended) A method for growing oxide thin films on a substrate in a reactor by the Atomic Layer Epitaxy (ALE) process alternately comprising at least three different growth cycles comprising saturating, self-limiting surface reactions on the substrate, wherein:

a first growth cycle comprises feeding a pulse of a cyclopentadienyl compound of strontium into the reactor;

purging the reactor with an inert gas;

feeding a pulse of a reactive oxygen precursor into the reactor; and

purging the reactor with an inert gas; and

a second growth cycle comprises feeding a pulse of a volatile titanium compound into the reactor;

purging the reactor with an inert gas;

feeding a pulse of a reactive oxygen precursor into the reactor; and

purging the reactor with an inert gas; and

a third growth cycle comprises feeding a pulse of a cyclopentadienyl compound of barium into the reactor;

purging the reactor with an inert gas;

feeding a pulse of a reactive oxygen precursor into the reactor; and

purging the reactor with an inert gas.

37. (Previously Presented) The method of Claim 36, wherein said method comprises repeating the first growth cycle, the second growth cycle, or the third growth cycle from 1 to 10 times in succession.

38. (Previously Presented) The method of Claim 37, wherein the ratio of the number of first growth cycles to the number of second growth cycles is 0.8 — 1.2.

39. (Previously Presented) The method of Claim 37, wherein the ratio of the number of third growth cycles to the number of second growth cycles is 0.8 — 1.2.

# Atomic layer epitaxy deposition processes

S. M. Bedair

Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695-7911

(Received 23 March 1993; accepted 20 September 1993)

Atomic layer epitaxy (ALE) is emerging as a promising epitaxial growth technique for thickness control at the atomic level. The article outlines recent progress in ALE of III-V and Si thin films. Also models describing the self-limiting processes will be outlined.

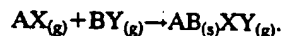
## I. INTRODUCTION

Recent progress in epitaxial growth technology has led research in semiconductor materials and devices to a new era. With the advent of the maturity of molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), ultrathin semiconductor materials can be prepared routinely. During the past decade, interest has increased rapidly in exploring new physics, chemistry, and materials science of heterostructures. Also novel optical and electrical devices based on quantum size effects have been fabricated, principally in III-V compounds. A new generation of heterostructural devices such as semiconductor lasers, resonant tunneling diodes (RTD), multiquantum well photodetectors, and high electron mobility transistors (HEMTs) were designed in accord with the newly developed artificial materials. These structures, however, require precise control in layer thickness and junction abruptness at heterointerfaces. Both MBE and MOCVD have been recognized techniques for the growth of ultrathin epitaxial layers; however, achieving the growth of two-dimensional (2D) heterostructures relies very much on preciseness in the control of growth parameters such as growth temperature, fluxes of source materials, and growth time. Nevertheless, in these two techniques, run-to-run reproducibility for the growth of ultrathin heterostructures becomes difficult due to the inevitable slight variations in growth parameters, which cause growth yield deterioration. Unfortunately, in fabricating 2D heterostructural devices like HEMTs and quantum well lasers, epilayer thickness uniformity and heterointerface abruptness are usually very critical. The demand for easier control of film thickness uniformity and heterojunction abruptness in growing sophisticated heterostructures encourages the resort to a growth process in which growth proceeds in monolayer-by-monolayer fashion.

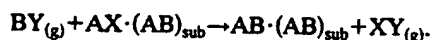
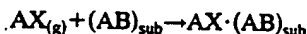
Atomic layer epitaxy (ALE) is a recently developed growth technique which has received much attention because of its unique digital growth process.<sup>1</sup> In contrast to MBE and MOCVD growth, in which reacting precursors are introduced simultaneously and reach the substrate surface together, ALE growth of III-V compounds, for example, proceeds by exposing the substrate surfaces to group III precursors in the absence of group V precursors, followed by exposing the substrate surface to group V precursors in the absence of group III precursors. Accordingly, the basic principle of ALE growth is based on alternating chemisorption, surface reaction, and desorption of the reactants. ALE growth is characterized by its self-limiting deposition

process,<sup>1-10</sup> in which the growth rate is independent of growth parameters such as vapor pressure of the precursors and growth temperature, but is dependent on the number of growth cycles and the lattice constant of the material. ALE also allows epitaxial growth of III-V compounds to proceed at low temperatures. As a consequence, ALE growth promises extremely uniform thickness and very good growth reproducibility of heterointerface abruptness for the grown films. These are difficult to achieve by conventional growth methods where all the reacting species are mixed together on top of the substrate. This growth approach is a potentially powerful growth technique for preparing epitaxial layers for ultrathin film devices.

We will now briefly discuss the mechanism of ALE growth. A general ALE reaction for growing compound AB from reactants AX and BY can be described as



The reaction can be divided into two steps:



In this case, gaseous AX chemisorbs on the compound AB surface, and the oncoming AX, which only weakly physisorbs on the  $AX \cdot (AB)_{sub}$ , will be removed. When another gaseous reactant BY is introduced, it reacts with the adsorbate AX chemisorbed on the AB substrate surface to form one monolayer of AB, and the gaseous reacting product XY is removed.

Various choices of  $AX_{(g)}$  and  $BY_{(g)}$  have been utilized for ALE growth. Among them are elements, metalorganics, metal-halides, hydrides, and so forth. Owing to differences in chemical properties between source materials, each individual ALE process may not follow the same reaction route, although the principle of ALE growth looks very straightforward. Consequently, caution must be used in the selection of reacting species since they also determine the detailed ALE process. In general, the greater the difference between the chemisorbed monolayer adsorbate's binding energy on the surface and the subsequent physisorbed species binding energy on the formed monolayers, the better the self-regulating characteristics of the ALE process will be. Because the source materials have to be volatile enough at normal growth temperatures and pressures, metalorganics, which are volatile in nature, are often preferred instead of elemental sources.

ALE growth of GaAs using TMGa and AsH<sub>3</sub> has been achieved in atmospheric MOCVD, low pressure MOCVD,



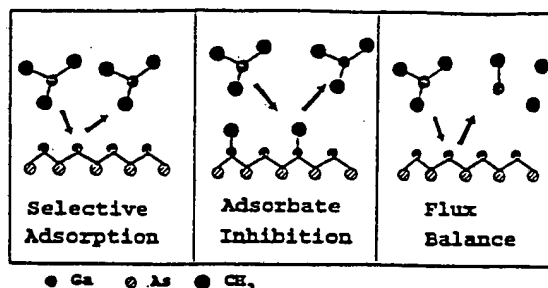


FIG. 1. Summary of three models, of ALE of GaAs using TMGa and AsH<sub>3</sub>: selective adsorption allows no TMGa decomposition on a Ga-covered surface. Adsorbate inhibition prohibits TMGa decomposition on a methyl covered surface. The flux balance requires a balance of adsorbing and desorbing methylgallium species.

and chemical-beam epitaxy (CBE) systems. The operating pressures ranged from 760 to 10<sup>-9</sup> Torr. Nishizawa *et al.*<sup>10</sup> utilized a CBE system for the growth of GaAs by the so-called molecular-layer epitaxy (MLE), in which monolayer deposition was achieved at 500 °C. Bedair *et al.*<sup>1</sup> achieved ALE growth of GaAs in a specially designed reactor and susceptor operated at atmospheric pressure; the self-limiting growth was achieved from 450 to 700 °C. DenBaars *et al.*<sup>6</sup> also achieved ALE growth at atmospheric pressure using a conventional MOCVD reactor with saturated monolayer growth being observed over the temperature range 445–485 °C. The Fujitsu group<sup>3</sup> achieved ALE growth using a low pressure MOCVD system with TMGa and AsH<sub>3</sub> being supplied as a fast pulsed gas stream from a jet nozzle, which

was found to be very effective in extending the monolayer limited growth window (460–550 °C). They called this particular setup pulsed-jet epitaxy (PJE).

## II. CURRENT PROPOSED ALE MODELS FOR III-V COMPOUNDS

The ALE growth process is characterized by the self limiting process, indicating the independence of the growth rate on the flux of the reactant gases. Several models were proposed and are summarized in Fig. 1.

(1) The selective adsorbate model<sup>11</sup> states that TMGa will not decompose on an atomic Ga-rich surface. It was supported by x-ray photoelectron spectroscopy (XPS) surface studies showing no carbon on TMGa dosed surfaces. However, XPS requires cooling and transport from the growth chamber to the XPS chamber, which is a significant change in the environment for the substrate. This model has been completely excluded by a study demonstrating TMGa decomposition on a Ga surface.<sup>12</sup>

(2) The adsorbate inhibition model will not allow decomposition of TMGa on a methylgallium species covered surface.<sup>13</sup> It is supported by temperature programmed desorption (TPD) studies showing the lifetime of the methyl radicals under ultrahigh vacuum (UHV) conditions. This is not the complete picture, however, since at higher growth temperatures the methyl lifetimes are much too short to explain our ability to maintain ML/cycle growth.

(3) The flux balance model<sup>14</sup> requires a balance to be maintained between desorbing monomethylgallium (MMGa) and adsorbing MMGa during the TMGa exposure. This

TABLE I. Summary of reported ALE growth conditions for GaAs with TMGa used as the gallium precursor.

Type of system pressure	Torr	Temperature range (°C)	Exposure time (s)	Reference
Vertical MOCVD rotating susceptibility	760	450–700	0.2–3/0.3 TMGa/AsH <sub>3</sub>	1
Vertical MOCVD rotating susceptibility	30	550–650	0.2–0.6/0.8/0.4/0.8 TMGa/purge/AsH <sub>3</sub>	2
Vertical chimney MOCVD	20	430–560	1–30/1–10 TMGa/AsH <sub>3</sub>	3
Vertical H <sup>+</sup> plasma MOCVD	20	430–500	3/2/2/2 TMGa/purge/AsH <sub>3</sub> /purge	4
Horizontal MOCVD	100	500	3/2/4–8/2 TMGa/purge/AsH <sub>3</sub> /purge	5
Horizontal MOCVD vent/run	100	T < 460	1/1/1/1 TMGa/purge/AsH <sub>3</sub> /purge	6
Horizontal MOCVD vent/run	760	450	0.6/1.5/1.5/0 TMGa/halt/AsH <sub>3</sub> /H <sub>2</sub> /purge	7
Horizontal MOCVD	70	490–500	1/3/1/3 TMGa/purge/AsH <sub>3</sub> /purge	8
UHV MOMBE		470	15–50/10/10/10 TMGa/evac/AsH <sub>3</sub> /evac	9
UHV MOMBE		500	4/3/20/3 TMGa/evac/AsH <sub>3</sub> /evac	10

seems to be an obvious requirement, but one which had been previously overlooked. There must be a compensation for desorbed MMGa from the surface, otherwise less than ML/cycle growth will result. However, the upper temperature limit of ALE growth has always been reported to be characterized by growth rates exceeding the ML/cycle; thus the flux balance model is not complete either.

None of these models completely explain the collection of ALE GaAs data published and presented in Table I. In this table, we listed reported ALE growth conditions for GaAs, using TMGa. From the table, a wide ALE temperature window was achieved by our group using the rotating substrate approach with provisions to reduce the gas phase reactions by shearing off the gas boundary layer. This window is wider than that achieved by other groups using near atmospheric pressure systems without any provision to reduce gas phase decomposition of TMGa. However, it seems that the UHV ALE approach where no gas phase decomposition occurs should yield a wider ALE window, which is not the case as shown in Table I. None of the available models specifically address why atmospheric pressure reactors can maintain ALE at temperatures far exceeding that of the UHV reactors,<sup>10</sup> where the gas decomposition is insignificant. In the following, we will discuss the main gas phase and surface reactions and try to explain, based upon a flux balance of methyl radicals near the substrate surface, why the rotating substrate approach can sustain ALE at higher temperatures.

### III. GAS PHASE REACTIONS

It is important to examine the gas phase decomposition of TMGa in  $H_2$  for an understanding of ALE in a MOCVD reactor. The region above the substrate where the temperature is high enough for decomposition of TMGa to occur is the chemical boundary layer.<sup>15</sup> Reactor conditions leading to the complete decomposition of TMGa in the gas phase represent the absolute limit of ALE in the MOCVD environment. Therefore, the characteristics of this chemical boundary layer and the time an incoming TMGa molecule spend in it are important reactor design issues.

The chemical boundary layer for TMGa established by the gas phase temperature at which it decomposes to Ga or other Ga species has been proposed to begin at 400 °C.<sup>16</sup> The thermal profile in the hydrogen carrier for the TMGa above the hot substrate is therefore critical for ALE in the MOCVD reactor. Since the rotating susceptor in our reactor cuts into a relatively cool  $H_2$  TMGa gas stream and then begins to heat this gaseous layer up to the substrate temperature, the thermal profile is transient. Estimates of these transient thermal profiles were made<sup>17</sup> for substrate temperatures of 500, 600, and 700 °C by solving the heat conduction equation for a flat plate at a given substrate temperature, heating  $H_2$  at a given height above the substrate ( $y$ ) as a function time. The boundary conditions are  $T_{hydrogen} = T_{substrate}$  at interface ( $y=0$ ) and  $T_{hydrogen} = 0$  °C as  $y \rightarrow \infty$ . The transient profiles are shown in Fig. 2 for substrate temperatures of 500, 600, and 700 °C. Pertinent TMGa exposure times are included to indicate the

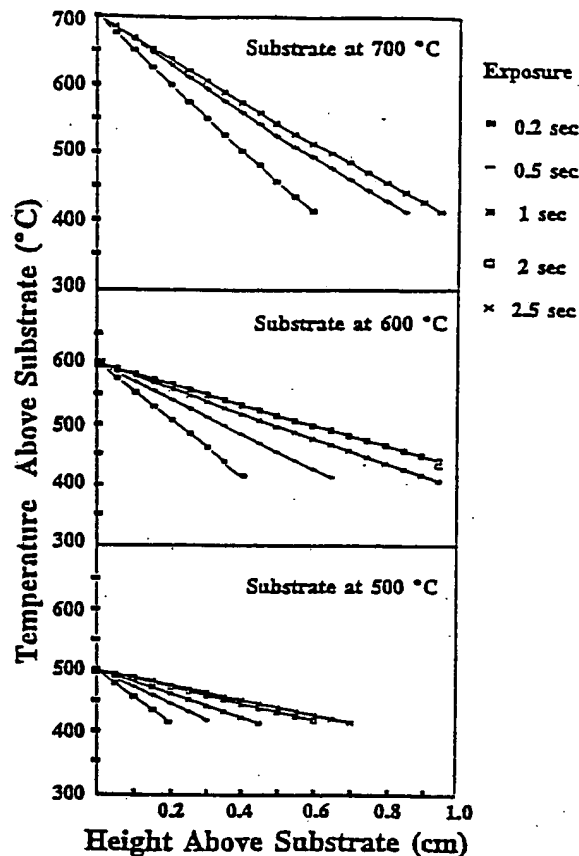


FIG. 2. Transient thermal profile in the  $H_2$  above the hot substrate for a substrate temperature of 500, 600, and 700 °C for several TMGa exposure times.

strong dependence of the gas phase thermal profile on exposure time increments of fractions of a second at high substrate temperatures. At a substrate temperature of 500 °C, for example, and a 0.2 s exposure to TMGa the gas phase temperature  $T_{hydrogen}$  is greater than 400 °C at a height of 0.25 cm above the substrate. As the substrate temperature is increased, the thermal profile expands and the chemical boundary layer gets thicker for the same exposure time to the TMGa/ $H_2$  stream. Another example is for a substrate temperature of 700 °C, as shown in Fig. 2. At this substrate temperature the thickness of the chemical boundary layer, where  $T_{hydrogen} \geq 400$  °C, has increased to 0.65 cm for a 0.2 s TMGa exposure. Therefore, the volume where gas phase decomposition of the TMGa molecule is more likely has increased, and the self-limiting characteristic at higher growth temperatures exhibits a narrower (on the order of fractions of a second) window of exposure times to the TMGa/ $H_2$  stream. However, in most other MOCVD reactors the effective TMGa exposure is 1 s or longer, making high temperature ALE difficult, as shown in Table I.

From the gas phase decomposition of TMGa arguments alone, the ALE temperature range in the UHV reactor should extend beyond that of the MOCVD. On the contrary, the UHV data demonstrate a narrower ALE temperature window than MOCVD, and this has been explained by the limitations

#### IV. METHYL RADICAL BALANCE MODEL

Based upon the system-dependent ALE temperature ranges and the above-mentioned gas phase and surface reactions, we propose the methyl radical balance as the self-limiting ALE mechanism. The surface must be stabilized with mono- or dimethylgallium molecules which are selective against chemisorption of TMGa. However, a balance between desorption of the methyl radicals from the monomethylgallium (MMGa) molecules at the surface and adsorption of methyls from the gas phase for the MOCVD type reactor is required during the TMGa exposure. The self-limiting ALE can be lost by two means, which may be a function of reactor type (pressure), growth temperature, and gas flux.

(1) If complete gas phase decomposition of incoming TMGa molecules leads to a surface covered with atomic gallium during the TMGa exposure, the surface of atomic gallium will not be self-limiting to further Ga or TMGa chemisorption.

(2) Methyls at the surface desorb faster than they can be replaced from the gaseous boundary layer, opening up sites of atomic Ga upon which TMGa can chemically adsorb. The desorption of MMGa is not a problem as long as there is a flux of TMGa to replace it, and as has been suggested, there is probably a balance of adsorbing MMGa and desorbing MMGa.<sup>12</sup> Thus the methyl radical balance model giving the condition for ALE self-limiting process can be simply stated as

$$\phi_{\text{gas}} > \phi_{\text{desorption}}$$

where  $\phi_{\text{gas}}$  is the  $\text{CH}_3$  flux impinging on the surface and is originated from the gas phase, and  $\phi_{\text{desorption}}$  is the desorption rate for  $\text{CH}_3$  from the  $\text{Ga}(\text{CH}_3)$  adsorbed species.

For the high vacuum case, the self-limiting state is determined by the lifetime of methyl radicals adsorbed at the surface in the mono- or dimethylgallium. There is no boundary layer to provide a source of replacement of methyl radicals, and desorbing methyl radicals are not likely to return to the surface since their mean-free-path is large. If MMGa desorbs it can simply be replaced by the incoming flux of TMGa. If a methyl desorbs for the surface MMGa molecule, however, the resulting Ga atom is no longer self-limiting against the incoming TMGa flux and the growth rate exceeds ML/cycle. Thus, ALE in the UHV environment probably has a temperature limit from the surface kinetics that cannot be circumvented.

MOCVD type reactors, however, should be able to extend the ALE temperature range by decreasing the TMGa exposure time to minimize gas phase decomposition and increasing the TMGa flux to achieve surface saturation faster.

#### V. CURRENT CHALLENGES FACING THE ALE TECHNIQUE AND RECENT III-V COMPOUNDS RESULTS

The ALE technique has suffered from several shortcomings that we believe have delayed its potential application and discouraged many researchers.<sup>18</sup> The first problem is very low growth rates, in some cases as low as  $0.02 \mu\text{m}$ . Some recent improvement in the growth rate was achieved and a growth rate of  $\sim 0.1 \mu\text{m/h}$  was reported, which we believe to be discouragingly slow. The main reason for such a low growth rate is the commonly used approach based on exposure/purging each of the reactants with a vent/run manifold configuration.<sup>3,6</sup> The finite gas reactor residence time and valve switching times will always lead to the growth of only a fraction of a  $\mu\text{m/h}$ . The approach we adopted in our laboratory<sup>1</sup> relies on rotating the substrate between the different source gas streams that are continuously flowing through a specially designed vertical reactor. The growth rate will depend on the substrate rotation speeds. Growth rates in the range of  $0.4\text{--}1 \mu\text{m/h}$  can be achieved with this approach.<sup>19</sup> Such growth rates are comparable with those reported by MBE.

The second problem facing ALE of III-V compounds is the high carbon background in the ALE grown films. Recently,<sup>19,20</sup> undoped GaAs with background electron concentrations in the high  $10^{14}/\text{cm}^3$  to low  $10^{15}/\text{cm}^3$  was grown in our laboratory. The liquid nitrogen temperature mobility was  $\sim 30\,000 \text{ cm}^2/\text{V s}$ , which is reasonably adequate for several devices. The device quality GaAs films were achieved by optimizing growth conditions such as growth temperature, flux of reactants and exposure times. Thus, we believe that at least for GaAs the ALE technique can provide films with convenient growth rates and good electrical properties.

Another problem facing ALE is the synthesis of ternary alloys such as AlGaAs and InGaAs required for heterostructures with different binary compounds. The problem with ternary alloys is the lack of compatible group III precursor that will adhere to the self-limiting process at the same growth temperature.<sup>21</sup>

Most of these difficulties have been addressed successfully using ALE growth system that relies on the rotating substrate approach.<sup>19,20</sup> Recent achievements in the III-compound area can be summarized as follows.

(1) ALE with growth rate  $\geq 2 \mu\text{m/h}$ .<sup>22</sup>

(2) ALE of device quality ternary alloys such as AlGaAs and InGaP.<sup>23,24</sup>

(3) ALE of several devices such as planar-doped field effect transistor,<sup>25</sup> heterojunction bipolar transistor,<sup>26</sup> storage capacitance,<sup>27</sup> and resonant tunnelling diodes.<sup>28</sup>

#### VI. ALE OF SILICON

For II-VI or III-V compound semiconductors, the ALE growth has been achieved by sequential injections of source gases containing respective components of semiconductor whose heterogeneous reactivities change with surface conditions.<sup>29</sup> On the other hand, group IV semiconductor are constructed with only one component. Therefore, ALE of group IV element consists of the two processes as follows.

The first step of ALE is the monolayer adsorption of partially decomposed source gas molecules over the clean surface. The adsorbate is constructed with a Si (or Ge) atom and another kind of atoms (or groups) bonded with Si (or Ge), such as  $\text{SiCl}_x$  or  $\text{Ge}(\text{CH}_3)_x$ . The Si (or Ge) atoms in adsorbates terminate the surface dangling bonds and make a grown monolayer, and the atoms (or group) such as Cl (or  $\text{CH}_3$ ) cover the newly grown layer surface. Therefore, when whole, the surface is covered by the adsorbates, monolayer growth is achieved. Successive source gas cannot be adsorbed chemically because the surface is completely covered and there are no dangling bonds. As a result, the growth is limited to 1 ML, that is, the self-limiting growth is achieved. The second step is the removal of the surface-terminating atoms (or groups) in some way.

Although many studies on the ALE of compound semiconductors were reported after the proposal of ALE in the 1970s,<sup>29</sup> the history of Si ALE has started in the last few years. First, successful ALE of Si has been reported by Nishizawa *et al.*<sup>30</sup> using dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ) as a source gas and hydrogen ( $\text{H}_2$ ) as a reducer gas.  $\text{SiH}_2\text{Cl}_2$  was decomposed into  $\text{SiCl}_x$ , and  $\text{SiCl}_x$  is adsorbed on the clean Si surface. The recovery of the clean surface was made by the reduction of surface-terminating Cl atoms by  $\text{H}_2$  to HCl. The growth temperature was, however, more than 815 °C for (100)Si and more than 890 °C for (111)Si. This temperature is too high to fabricate new materials and structures such as Si-Ge heterojunction or superlattices because of the diffusion of Si and Ge.

Two possible ways to lower the substrate temperature exist. The first way is the use of higher silane as a source gas, where surface-terminating atoms are H atoms instead of Cl atoms. H atoms terminating the Si surface are well known to be thermally desorbed from the Si surface at ~600 °C which is much lower than for Cl atoms.<sup>31</sup> Therefore, repetition of the injection of higher silane as a source gas and heating up the substrate for thermal desorption of H atoms can result in ALE. The second method is to use atomic H to reduce the surface terminating Cl atoms. The two approaches will be discussed in detail in the following sections.

## VII. UV-PHOTOASSISTED SI ALE

This approach was developed by Greene and co-workers.<sup>32</sup> This approach relies on the self-limiting adsorption of  $\text{Si}_2\text{H}_6$  at temperature ( $T$ ) below the  $\text{H}_2$  desorption temperature, followed by a rapid photothermal heating with an excimer laser pulse to desorb the surface hydrogen. Results<sup>33</sup> can be summarized as follows. Figure 3 shows the film growth rate  $R$  as a function of the steady-state substrate temperature  $T_s$  with and without pulsed laser irradiation during each deposition cycle. The peak pressure during the 1 s  $\text{Si}_2\text{H}_6$  exposures was 1.5 Torr, sufficient to reach surface saturation, as shown below, in all experiments. The maximum KrF laser energy density  $E_{\text{max}}$  at the sample surface in the irradiation experiments was decreased from 470 to 250  $\text{mJ cm}^{-2}$  as  $T_s$  was increased from 130 to 550 °C. The energy density window  $\Delta E$  over which  $R$  was found to be constant for a given,  $T_s = 150 \text{ mJ cm}^{-2}$ .  $R$  in Fig. 3 is plotted in units of ML per growth cycle, where 1 ML in the [001]

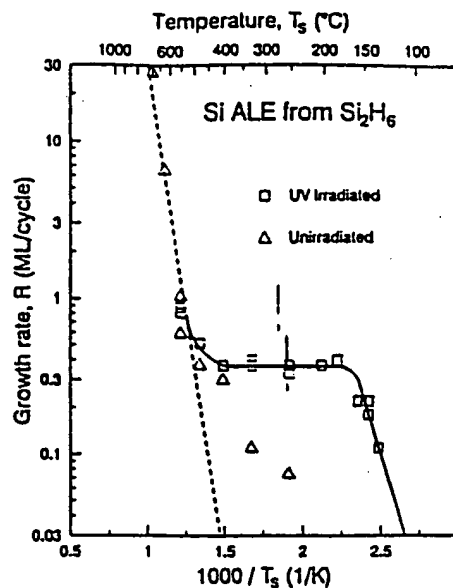


FIG. 3. Si growth rate  $R$  as a function of substrate temperature  $T_s$ .

direction is taken to be  $6.8 \times 10^{14} \text{ cm}^{-2}$  corresponding to a thickness of 0.136 nm. For the unirradiated films,  $R$  varied exponentially with  $-1/T_s$  at  $T_s \geq 550$  °C yielding an apparent activation energy of 1.2 eV. At lower temperatures, the slope is reduced, and no measurable growth occurred at  $T_s$  below 200 °C. Films deposited with  $T_s \geq 625$  °C were smooth, high-quality epitaxial layers, as judged by reflection high-energy electron diffraction (RHEED), while films deposited at lower temperatures exhibited three-dimensional RHEED patterns with increased diffuse background intensity indicative of residual disorder.

In contrast, all films deposited at low temperatures with pulsed UV laser irradiation were smooth and well ordered, as judged by both RHEED and transmission electron microscopy, and exhibited much higher deposition rates at  $T_s \leq 400$  °C.<sup>33</sup> In fact, at  $T_s = 250$  °C,  $R$  increased by more than an order of magnitude in the presence of laser irradiation. Moreover, there is a range in growth temperatures between ~180 and 400 °C over which  $R$  is independent of  $T_s$ , and deposition proceeds by a kinetically self-limited ALE mechanism with no apparent activation barrier. Varying the number of laser pulses per cycle from 10 to 50 also had no effect on  $R$  which remained constant at ~0.4 ML/cycle. For  $T_s > 400$  °C, the growth rate of the laser irradiated films increases with increasing  $T_s$ , as deposition due to thermal pyrolysis begins to compete with ALE. At  $T_s < 180$  °C,  $R$  decreases with an apparent activation energy of ~0.5 eV.

The film growth rate as a function of the peak  $\text{Si}_2\text{H}_6$  pressure  $P$  during a 1 s exposure with  $T_s = 250$  °C,  $E = 400 \text{ mJ cm}^{-2}$ , and  $n_p = 10$  pulses is shown in Fig. 4. Measurable  $R$  values were obtained for  $P \geq 0.1 \text{ mTorr}$  and saturation was observed at  $P_{\text{sat}} \approx 1.5 \text{ mTorr}$  with  $R \approx 0.4 \text{ ML/cycle}$ . These results are further evidence of a self-limited kinetic growth mechanism. The  $\text{Si}_2\text{H}_6$  saturation exposure in Fig. 4 is in good agreement with the exposure required to obtain a satu-

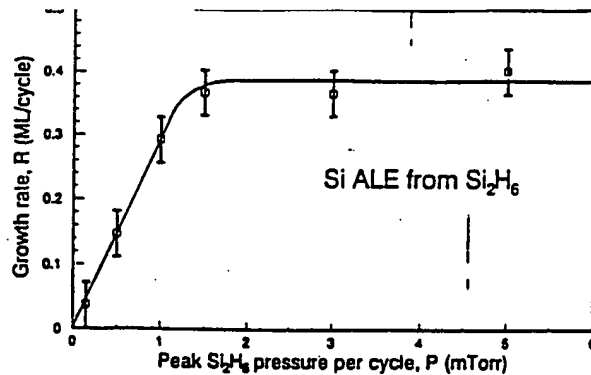


FIG. 4. Si growth rate  $R$  as a function of the maximum chamber pressure  $P$  during the  $\text{Si}_2\text{H}_6$  gas pulse. The film growth temperature  $T_s$  was  $250^\circ\text{C}$ , the KrF irradiation energy density  $E$  was  $400\text{ mJ cm}^{-2}$ , and the number of laser pulses per gas pulse  $n_p$  was 10.

rated  $(1\times 1)::2\text{H}$  dihydride surface during  $\text{Si}_2\text{H}_6$  adsorption experiments at room temperature.<sup>34</sup> However, the incident flux, and hence the time of exposure, in the latter case was  $\sim 4$  orders of magnitude lower than that employed in the present growth kinetics experiments.

The ALE growth rate was also found to be constant for a wide range in incident UV energy densities. While  $\Delta E$  remained  $\sim 150\text{ mJ cm}^{-2}$ ,  $E_{\text{max}}$  had to be decreased as the substrate temperature increased in order to achieve the same peak temperatures. In all cases, the laser-induced temperature was sufficient to cause complete removal of the hydrogen but less than that required for melting. One-dimensional heat-flow calculations, based upon optical absorption and incorporating temperature-dependent thermal parameters,<sup>35</sup> were used to estimate the melting threshold as a function of  $T_s$  and  $E$ . For 22 ns KrF irradiation, the  $1/e$  absorption depth is  $\sim 5.6\text{ nm}$  and the threshold energy density for melting was found to vary from 480 to  $410\text{ mJ cm}^{-2}$  as  $T_s$  was increased from  $250$  to  $400^\circ\text{C}$ . At  $T_s=250^\circ\text{C}$ , ALE growth with  $R\sim 0.4\text{ ML}$  per growth cycle was obtained for  $300 < E < 470\text{ mJ cm}^{-2}$ , while for  $T_s=400^\circ\text{C}$  the measured useable  $E$  range was  $220\text{--}365\text{ mJ cm}^{-2}$ .

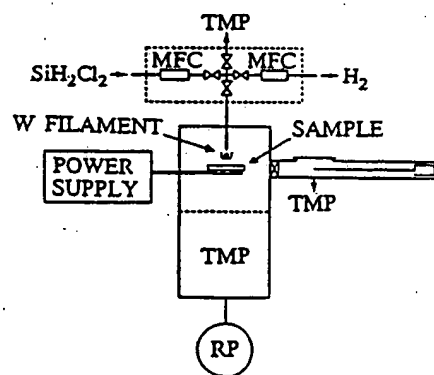


FIG. 5. Schematic view of ALE system using  $\text{SiH}_2\text{Cl}_2$  and atomic H.

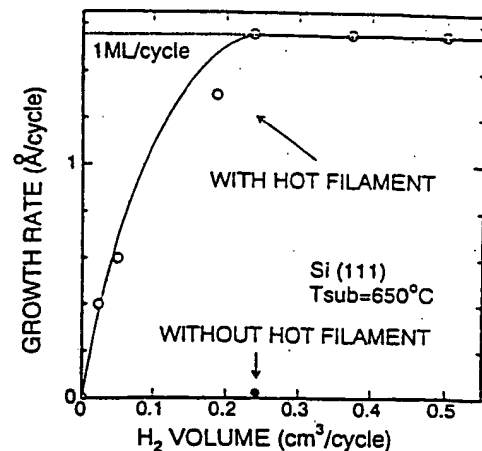


FIG. 6. Thickness per unit ALE cycle as a function of the  $\text{H}_2$  gas volume within an ALE cycle.

## VIII. ALE OF SILICON USING ATOMIC HYDROGEN

The second way to is to use  $\text{SiH}_2\text{Cl}_2$  with a reducer much more active than  $\text{H}_2$ . The use of atomic hydrogen (H) as a reducer in Si ALE growth was reported.<sup>36</sup> H atoms are able to be created easily and plasma-freely by decomposition of  $\text{H}_2$  using an incandescent tungsten filament.<sup>37,38</sup> Si ALE growth by sequential exposures into  $\text{SiH}_2\text{Cl}_2$  as a source gas and H as a reducer gas was successfully reported<sup>36</sup> and ideal monolayer growth per cycle has been demonstrated at  $540^\circ\text{C}$ . The ALE system used in their experiment was assembled as shown in Fig. 5. Figure 6 shows the growth rate as a function of the injected  $\text{H}_2$  gas volume per cycle with the substrate temperature of  $650^\circ\text{C}$ .<sup>36</sup> When the filament was not used, no growth occurred, however, with the filament, the growth rate increased with  $\text{H}_2$  volume. This means that H atoms were effective for Cl reduction at low temperatures. Reaching  $1\text{ ML/cycle}$ , the growth rate was saturated, i.e., the ALE growth was achieved in spite of very low substrate

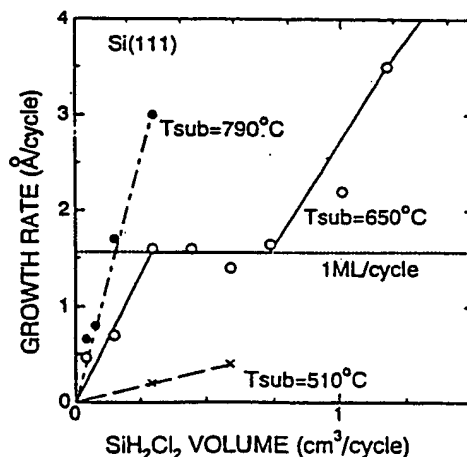


FIG. 7. Thickness per unit ALE cycle as a function of the  $\text{SiH}_2\text{Cl}_2$  gas volume within an ALE cycle.

temperatures. Figure 7 shows the growth rate as a function of the  $\text{SiH}_2\text{Cl}_2$  gas volume at the substrate temperatures of 520, 650, and 790 °C.<sup>36</sup> Only the  $\text{SiH}_2\text{Cl}_2$  gas flow rate was changed and other parameters were kept constant. At 520 °C, the growth rate increased with the gas volume, but was less than 1 ML/cycle. At 650 °C, the growth rate increased up to 1 ML/cycle with the gas volume and is saturated. In this saturation region, ALE growth was achieved. At 790 °C, the growth rate increased over 1 ML/cycle with no clear saturation.

## IX. CONCLUSIONS

ALE growth of III-V and silicon has been outlined. Self-limited processes have been observed in both cases. ALE of III-V compounds has produced device quality films and state-of-the-art devices. The quality of ALE Si films is not yet known.

## ACKNOWLEDGMENTS

The authors would like to thank ONR/SDIO, NSF, and NREL for partial support for this work.

- <sup>1</sup>S. M. Bedair, M. A. Tischler, T. Katsuyami and N. A. El-Masry, *Appl. Phys. Lett.* **47**, 51 (1985).
- <sup>2</sup>P. C. Colter, S. A. Hussien, A. Dip, M. U. Erdogan, W. M. Duncan, and S. M. Bedair, *Appl. Phys. Lett.* **59**, 1440 (1991).
- <sup>3</sup>M. Ozeki, K. Mochizuki, N. Ohtsuka, and K. Kodama, *J. Vac. Sci. Technol.* **5**, 1184 (1987).
- <sup>4</sup>M. de Keijser and C. van Opdorp, *Appl. Phys. Lett.* **58**, 1184 (1991).
- <sup>5</sup>A. Usui and H. Watanabe, *Third International Conference on Modulated Semiconductor Structures*, Montpellier, France, 1987 (unpublished).
- <sup>6</sup>S. DenBaars, A. Hariz, C. Beyler, B. Maa, Q. Chen, and P. Dapkus, *Mater. Res. Soc. Symp. Proc.* **102**, 527 (1988).
- <sup>7</sup>E. Colas, R. Bhat, and B. Skromme, *Appl. Phys. Lett.* **55**, 2769 (1989).
- <sup>8</sup>H. Yokoyama, M. Shinohara, and N. Inoue, *Appl. Phys. Lett.* **59**, 2148 (1991).
- <sup>9</sup>A. Watanabe, T. Isu, M. Hata, T. Kamijoh, and Y. Katayama, *Jpn. J. Appl. Phys.* **L1080** (1989).
- <sup>10</sup>J. Nishizawa, H. Abe, and T. Kurabayashi, *J. Electrochem. Soc.* **132**, 1197 (1985).
- <sup>11</sup>K. Kodama, M. Ozeki, K. Mochizuki, and N. Ohtsuka, *Appl. Phys. Lett.* **54**, 656 (1989).
- <sup>12</sup>J. R. Creighton, K. R. Lykke, V. A. Shamamian, and B. D. Kay, *Appl. Phys. Lett.* **57**, 279 (1990).
- <sup>13</sup>J. Nishizawa and T. Kurabayashi, *J. Cryst. Growth* **93**, 98 (1988).
- <sup>14</sup>*Chemical Perspectives of Microelectronic Materials II*, edited by M. L. Yu, U. Memmert, N. I. Buchan, and T. F. Keuch, L. V. Interrante, K. F. Jensen, L. H. Dubois, and M. E. Gross (Materials Research Society, Pittsburgh, PA, 1991), Vol. 204.
- <sup>15</sup>M. H. J. M. de Croon and L. J. Giling, *J. Electrochem. Soc.* **137**, 2867 (1990).
- <sup>16</sup>J. Nishizawa and T. Kurabayashi, *J. Electrochem. Soc.* **130**, 413 (1983).
- <sup>17</sup>K. G. Reid, A. F. Myers, N. A. El-Masry, and S. M. Bedair, *Thin Solid Films* **225**, 59 (1993).
- <sup>18</sup>S. M. Bedair, *Acta Polytech. Scand.* **195**, 17 (1990).
- <sup>19</sup>P. C. Colter, S. A. Hussien, A. Dip, M. U. Erdogan, W. M. Duncan, and S. M. Bedair, *Appl. Phys. Lett.* **59**, 12 (1991).
- <sup>20</sup>J. R. Gong, P. Colter, D. Jung, S. Hussien, C. Parker, A. Dip, W. Duncan, and S. M. Bedair, *J. Cryst. Growth*, **107**, 83 (1990).
- <sup>21</sup>W. Jeong, E. Menu, and P. D. Dapkus, *Appl. Phys. Lett.* **55**, 244 (1989).
- <sup>22</sup>A. Dip, G. Eldallal, P. Colter, and S. M. Bedair, *Appl. Phys. Lett.* **62**, 2378 (1993).
- <sup>23</sup>A. Dip, G. Eldallal, P. Colter, and S. M. Bedair, *Thin Solid Films* **225**, 109 (1993).
- <sup>24</sup>B. McDermott, N. El-Masry, F. Hyuga, and S. M. Bedair, *J. Cryst. Growth* **107**, 96 (1991).
- <sup>25</sup>M. Hashemi, B. McDermott, U. Meshra, J. Ramdani, A. Morris, J. Hauser, and S. M. Bedair, *IEEE Trans. Electron Device Lett.* **EDL-12**, 258 (1991).
- <sup>26</sup>T. Henderson, B. Bayraktaroglu, S. Hussien, A. Dip, P. Colter, and S. M. Bedair, *Electron Lett.* **27**, 692 (1991).
- <sup>27</sup>S. M. Bedair, B. McDermott, K. Reid, P. Neudeck, J. Cooper, and M. Melloch, *IEEE Trans. Electron Device Lett.* **EDL-11**, 261 (1990).
- <sup>28</sup>A. C. Seabaugh, J. H. Luscombe, J. N. Randall, P. C. Colter, A. Dip, G. Eldallal, and S. M. Bedair, *Thin Solid Films* **225**, 99 (1993).
- <sup>29</sup>T. Suntola and M. J. Antson, U. S. Patent No. 4058430 (1977).
- <sup>30</sup>J. Nishizawa, K. Aoki, S. Suzuki, and K. Kikuchi, *J. Cryst. Growth* **99**, 502 (1990).
- <sup>31</sup>G. Schulze and M. Henzler, *Surf. Sci.* **124**, 336 (1983).
- <sup>32</sup>Y. Suda, L. Lubben, T. Motooka, and J. E. Greene, *J. Vac. Sci. Technol. B* **7**, 1171 (1990).
- <sup>33</sup>D. Lubben, R. Tsu, T. R. Bramblett, and J. E. Greene, *Mater. Res. Soc. Symp. Proc.* **22**, 177 (1991).
- <sup>34</sup>Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, *J. Vac. Sci. Technol. A* **8**, 61 (1990).
- <sup>35</sup>K. Suzuki, D. Lubben, and J. E. Greene, *J. Appl. Phys.* **58**, 979 (1985).
- <sup>36</sup>S. Imai, T. Iizuka, O. Sugiura, and M. Matsura, *Thin Solid Films* **225**, 168 (1993).
- <sup>37</sup>I. Langmuir, *J. Amer. Chem. Soc.* **34**, 860 (1912).
- <sup>38</sup>O. Sugiura, T. Shiraiwa, H. Kanoh, and M. Matsumura, *Mater. Res. Soc. Symp. Proc.* **258** (1992).

Growth of SrTiO<sub>3</sub> and BaTiO<sub>3</sub> Thin Films by Atomic Layer DepositionMarko Vehkamäki, Timo Hatanpää, Timo Hänninen, Mikko Ritala,\*<sup>2</sup> and Markku Leskelä

Department of Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland

SrTiO<sub>3</sub> and BaTiO<sub>3</sub> thin films were deposited by atomic layer deposition making use of a novel class of strontium and barium precursors, i.e., their cyclopentadienyl compounds, together with titanium tetraisopropoxide and water. SrTiO<sub>3</sub> films were grown at 325°C from strontium bis(trisopropylcyclopentadienyl) and BaTiO<sub>3</sub> at 275°C from barium bis(pentamethylcyclopentadienyl). After annealing in air at 500°C, permittivities of 180 and 165 were measured for SrTiO<sub>3</sub> and BaTiO<sub>3</sub>, respectively. The films showed excellent conformality and complete filling of test trench structures.

© 1999 The Electrochemical Society, S1099-0062(99)05-021-X. All rights reserved.

Manuscript received May 5, 1999. Available electronically August 5, 1999.

Thin films of SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, and (Ba<sub>1-x</sub>Sr<sub>x</sub>)TiO<sub>3</sub> have been extensively examined because of their potential use as high permittivity dielectric materials in future generation dynamic random access memory (DRAM) capacitors.<sup>1,2</sup> Although these materials have much higher permittivities than the traditionally used SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> or the intermediate permittivity Ta<sub>2</sub>O<sub>5</sub>, it is foreseen that even with these materials the storage capacities required for the high density memories can be achieved only with three-dimensional storage node geometries. Therefore, good conformality is required from the thin film deposition process. In comparison with the physical vapor deposition (PVD) techniques, chemical vapor deposition (CVD) is capable of much better conformality and has therefore gained a lot of interest in making strontium and barium titanate thin films.<sup>3-5</sup> In CVD, excellent conformality is achieved when the process is carried out at a temperature low enough that the surface reactions are the rate-limiting step in the film growth. At higher temperatures the precursor transportation becomes the limiting factor, causing a degradation of the conformality.

Atomic layer deposition (ALD), also known as atomic layer epitaxy (ALE), can give conformality equal, and often superior, to that of CVD.<sup>6</sup> The key features of ALD are the alternate supply of the precursors and saturation of the surface reactions between the sequentially dosed precursors.<sup>7-10</sup> Under such conditions the film growth is self-limiting, ensuring not only excellent conformality but also good large area uniformity plus simple and accurate film thickness control. Furthermore, due to the alternate dosing of the precursors, detrimental gas-phase reactions are inherently eliminated. However, no true ALD process for SrTiO<sub>3</sub> or BaTiO<sub>3</sub> has yet been developed. This is evidently because the selection of strontium and barium precursors has been limited to their  $\beta$ -diketonate compounds. Though Sr<sup>11-13</sup> and Ba<sup>11,14</sup> films have been deposited by ALD from Sr(thd)<sub>2</sub> (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione), Ba(thd)<sub>2</sub>, and H<sub>2</sub>S, these Sr and Ba compounds do not react with water or oxygen in ALD processes at temperatures low enough so that they, or the commonly used titanium precursor titanium tetraisopropoxide (Ti(O-*i*-Pr)<sub>4</sub>), would not self-decompose thermally and thereby destroy the self-limiting growth mechanism. Sr(thd)<sub>2</sub> does react with ozone at around 300°C but the resulting film is SrCO<sub>3</sub> or, when combined with titanium, an amorphous mixture which needs to be annealed at 700°C to obtain crystallized SrTiO<sub>3</sub>.<sup>15</sup> In this paper, we report ALD of SrTiO<sub>3</sub> and BaTiO<sub>3</sub> using novel precursors for strontium and barium, i.e., their cyclopentadienyl compounds, which have generally been considered too pyrophoric for convenient use and handling. Our experience shows, however, that these compounds can be used without any major difficulty and can be exposed to air for a short time for loading into the reactor.

## Experimental

SrTiO<sub>3</sub> and BaTiO<sub>3</sub> films were deposited on glass substrates in a flow-type F-120 ALE reactor (Microchemistry Ltd, Espoo,

Finland)<sup>10</sup> operated under a pressure of about 10 mbar. Nitrogen made on site by a Schmidlin NG3000 nitrogen generator (rated purity of 99.9995 %) was used as a carrier and purging gas. Strontium bis(trisopropylcyclopentadienyl) [Sr(C<sub>5</sub>-*i*-Pr<sub>3</sub>H<sub>2</sub>)<sub>2</sub>]<sup>16</sup> and barium bis(pentamethylcyclopentadienyl) [Ba(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>17</sup> were synthesized according to the methods described in the literature and were obtained in a form where tetrahydrofuran (THF) solvent molecules were coordinated to the metals as adduct ligands. However, while evacuated and heated in the reactor, the THF ligands were most likely completely released before the process. Ti(O-*i*-Pr)<sub>4</sub> (Aldrich, 97 %) and water were used as the other precursors. The metal precursors were evaporated inside the reactor at temperatures of 40°C for Ti(O-*i*-Pr)<sub>4</sub>, 100°C for Sr(C<sub>5</sub>-*i*-Pr<sub>3</sub>H<sub>2</sub>)<sub>2</sub>, and 160°C for Ba(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, and pulsed by inert gas valving.<sup>10</sup> Water vapor was led into the reactor from an external reservoir held at room temperature. The pulse times were 0.6 s while the purge time was 0.5 s.

For electrical measurements the films were deposited on indium-tin oxide (ITO) electrodes and covered with Al electrodes forming capacitors with an area of 0.12 cm<sup>2</sup>. Before the Al electrode deposition the films were annealed in air at 500°C for 1 h. Capacitances were measured at a frequency of 10 kHz with an HP4275 multifrequency LCR meter and the dc leakage currents with an Autolab potentiostat. Film thicknesses were determined by fitting<sup>18</sup> the optical transmittance spectra measured within a wavelength range of 370-1100 nm. Film crystallinity was measured with a Philips MPD 1880 X-ray diffractometer (XRD).

## Results and Discussion

The earlier study<sup>19</sup> on ALD growth of TiO<sub>2</sub> from Ti(O-*i*-Pr)<sub>4</sub> indicated that self-limiting film growth may be achieved at and below 325°C above which significant self-decomposition of Ti(O-*i*-Pr)<sub>4</sub> began. Therefore, the growth temperatures chosen for this study were 250-325°C. The film compositions were varied by varying the ratio of Sr-O and Ti-O deposition cycles. These deposition cycles consisted of sequential exposure of the Sr precursor and water, and Ti(O-*i*-Pr)<sub>4</sub> and water, respectively, and were mixed with each other as completely as possible. The growth rate of SrTiO<sub>3</sub> increased linearly with increasing Sr/Ti cycle ratio from 0.7 Å/cycle (Sr/Ti = 0.67) to 1.8 Å/cycle (Sr/Ti = 1.5). Figure 1 shows the permittivity and composition of SrTiO<sub>3</sub> films as a function of the Sr to Ti cycle ratio. The optimum cycle ratio is 0.67-0.82 which results in a Sr/Ti elemental ratio of about 1 and a permittivity of 170-180. Without the postannealing in air at 500°C the permittivities were much lower in the range of 90 for the optimum Sr/Ti cycle ratios. For comparison, permittivities of 210 have been obtained for SrTiO<sub>3</sub> films grown by CVD but the deposition and annealing temperatures have been higher, in the range of 550 to 750°C, than those used in the present study.<sup>20,21</sup>

Figure 2 shows the XRD diffractograms of the film with the highest permittivity as-deposited and after annealing. In both cases rather strong (100) orientation is observed. No significant increase in the reflection intensities is caused by the annealing but, rather, their positions shift somewhat corresponding to a lattice parameter

\* Electrochemical Society Active Member.

<sup>2</sup> E-mail: Mikko.Ritala@Helsinki.fi

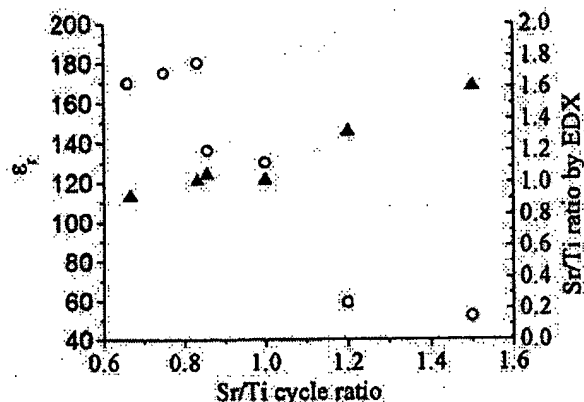


Figure 1. Sr/Ti ratio ( $\Delta$ ) and permittivity (O) of  $\text{SrTiO}_3$  films deposited at  $325^\circ\text{C}$  as a function of the  $\text{Sr}(\text{C}_5\text{-i-Pr})_2\text{-H}_2\text{O}$  to  $\text{Ti}(\text{O-i-Pr})_2\text{-H}_2\text{O}$  cycle ratio. The film composition was measured by energy dispersive X-ray spectroscopy and independently verified by Rutherford backscattering spectrometry.

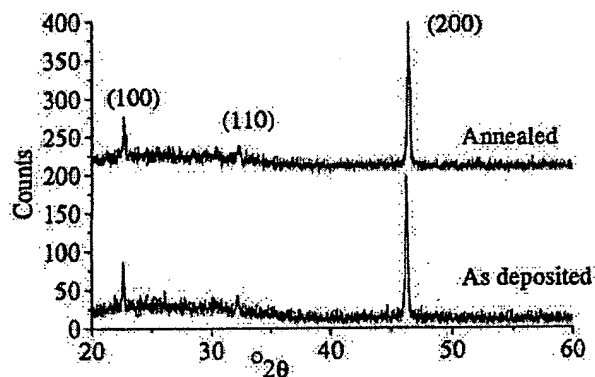


Figure 2. XRD diffractograms of the as-deposited and annealed  $\text{SrTiO}_3$  film grown with a Sr/Ti cycle ratio of 0.82.

change from 3.931 to 3.917 Å, to be compared with 3.905 Å given in the XRD reference data.<sup>22</sup>

As commonly observed with  $\text{SrTiO}_3$  thin films, the permittivity decreased with decreasing film thickness. Anyhow, by a careful optimization of the Sr/Ti cycle ratio a permittivity of 100 could be achieved also with 50 nm  $\text{SrTiO}_3$  films. Nevertheless, either higher temperature annealing or two-step deposition starting with a thin well-crystallized seed layer will be needed to increase the permittivities of the thinnest films.

The leakage currents through the ITO- $\text{SrTiO}_3$ -Al capacitors were rather high:  $2 \times 10^{-6}$  and  $5 \times 10^{-4}$  A/cm<sup>2</sup> for negatively and positively biased Al, respectively, when 1 V potential was applied across about 400 nm thick film. Since the main conduction mechanism in  $\text{SrTiO}_3$  films is thermionic emission,<sup>23</sup> our electrode materials with small work functions (Al 3.74 eV,<sup>23</sup> ITO 4.4-4.5 eV<sup>24</sup>) are apparently not ideal for achieving low leakage currents. It will be a topic of future work to examine high work function electrode materials for reducing the leakage current.

The conformality of the ALD-made  $\text{SrTiO}_3$  films was examined with test structures patterned on silicon wafers. As characteristic of ALD,<sup>6</sup> excellent conformality was obtained also with deep trenches (Fig. 3a). Though in the memory capacitor applications complete trench filling is not required, this was examined here since it serves as the ultimate test for the conformal deposition capability. As seen in Fig. 3b, complete trench filling without key hole formation could be achieved with the ALD  $\text{SrTiO}_3$  process. These images indicate also that the films consist of columnar grains the width of which is nearly equal to their height. The film microstructure looks somewhat porous in the trenches but it is hard to say whether this is real or due

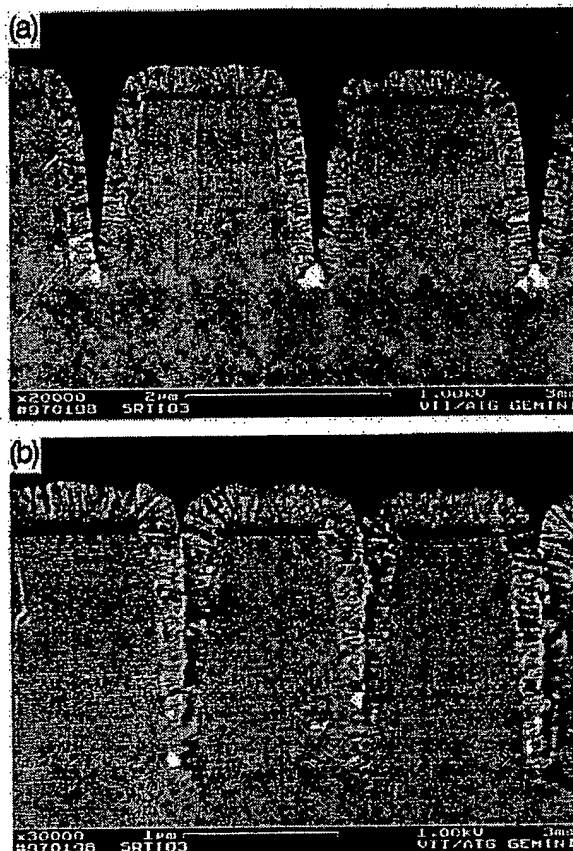
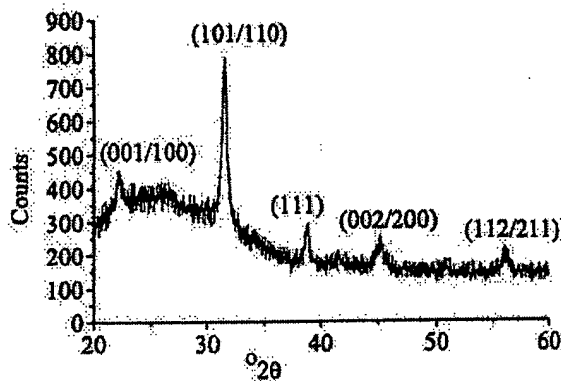


Figure 3. Cross-sectional SEM images of silicon wafer test structures showing the excellent (a) conformality and (b) trench filling capability of the ALD  $\text{SrTiO}_3$  process. Note that on the silicon top surface there is about 100 nm thermal silicon oxide layer between the  $\text{SrTiO}_3$  film and the substrate.

to a fracture of the ceramic film during sample preparation.

$\text{BaTiO}_3$  films were deposited analogously from  $\text{Ba}(\text{C}_5\text{Me}_5)_2$ ,  $\text{Ti}(\text{O-i-Pr})_4$ , and  $\text{H}_2\text{O}$ . The deposition temperature was kept somewhat lower at  $275^\circ\text{C}$  because of thermal decomposition of  $\text{Ba}(\text{C}_5\text{Me}_5)_2$ . The deposition rates were about 0.5 Å/cycle. As compared with the  $\text{SrTiO}_3$  process, the  $\text{BaTiO}_3$  process had more problems in reproducibility of the film composition and, thereby, of the permittivity as well. Nevertheless, when the process was optimized to result in the Ba/Ti ratio close to 1, permittivities of about 165 were measured for the annealed films. The as-deposited  $\text{BaTiO}_3$  films were essentially amorphous, and also the annealed films gave weaker and broader XRD reflections (Fig. 4) as compared with the  $\text{SrTiO}_3$  films. Obviously, the deposition and annealing temperatures used were not high enough for achieving well-crystallized  $\text{BaTiO}_3$ . The deposition temperature cannot be increased much because of the thermal stability of  $\text{Ba}(\text{C}_5\text{Me}_5)_2$ , but a replacement of the glass substrates used in this study with substrates tolerating higher annealing temperatures will make it possible to examine if higher permittivities can be reached. On the other hand, by modifying the cyclopentadienyl type ligand, better thermal stability can be looked for. The permittivities of the  $\text{BaTiO}_3$  films grown by CVD have varied over a wide range. While permittivities as high as 1100 were achieved with films made by plasma CVD at about  $600^\circ\text{C}$ ,<sup>25</sup> also lower values have been reported, e.g., 107 for the film grown at  $700^\circ\text{C}$ .<sup>26</sup> On the other hand, the  $\text{BaTiO}_3$  films deposited with local epitaxy onto InSb<sup>27</sup> and InP<sup>28</sup> at  $300^\circ\text{C}$  had significantly different permittivities of 743 and 78, respectively. The amorphous  $\text{BaTiO}_3$  films obtained by CVD below  $550^\circ\text{C}$  had a permittivity of only 13.<sup>29</sup>



Figure 4: XRD diffractogram of the annealed BaTiO<sub>3</sub> film.

### Acknowledgments

The authors thank Dr. Eero Rauhala for the RBS measurements and also Dr. Esko Kauppinen, Dr. Unto Tapper, and Petri Ahonen for access to and assistance with the SEM imaging. Financial support from the Academy of Finland and the Technology Development Centre of Finland (TEKES) is gratefully acknowledged.

The University of Helsinki assisted in meeting the publication costs of this article.

### References

1. A. I. Kingon, S. K. Streiffer, C. Basceri, and R. K. Summerfelt, *MRS Bull.*, 46 (July 1996).
2. C. S. Hwang, *Mater. Sci. Eng. B*, 56, 178 (1998).
3. S. M. Bilodeau, R. Carl, P. Van Buskirk, and J. Ward, *Solid State Technol.*, 235 (July 1997).
4. P. C. Van Buskirk, S. M. Bilodeau, I. F. Roeder, and P. S. Kirlin, *Jpn. J. Appl. Phys.*, 35, 2520 (1996).
5. C. M. Foster, in *Thin Film Ferroelectric Materials and Devices*, R. Ramis, Editor, p. 167, Kluwer, Boston (1997).
6. M. Ritala, M. Leskellä, J.-P. Dekker, C. Mutsaers, P. J. Soininen, and J. Skarp, *Chem. Vap. Deposition*, 5, 7 (1999).
7. M. Leskellä and M. Ritala, *J. Phys. IV*, 5, C5 (1995).
8. M. Ritala, *Appl. Surf. Sci.*, 112, 223 (1997).
9. L. Niinistö, M. Ritala, and M. Leskellä, *Mater. Sci. Eng. B*, 41, 23 (1996).
10. T. Suntola, *Thin Solid Films*, 216, 84 (1992).
11. M. Tammenmaa, H. Antson, M. Asplund, L. Hiltunen, M. Leskellä, L. Niinistö, and E. Ristolainen, *J. Cryst. Growth*, 84, 151 (1987).
12. M. Leskellä, L. Niinistö, E. Nykänen, P. Soininen, and M. Tiitola, *Mater. Res. Soc. Symp. Proc.*, 222, 315 (1991).
13. P. Soininen, E. Nykänen, L. Niinistö, and M. Leskellä, *Chem. Vap. Deposition*, 2, 69 (1996).
14. V. Saanila, J. Ihanus, M. Ritala, and M. Leskellä, *Chem. Vap. Deposition*, 4, 227 (1998).
15. A. Kosola and M. Pitkunen, Private communication.
16. D. J. Burkey, R. A. Williams, and T. P. Hanusa, *Organometallics*, 12, 1831 (1993).
17. C. J. Burns and K. A. Andersen, *J. Organomet. Chem.*, 325, 31 (1987).
18. M. Ylilammi and T. Ranta-aho, *Thin Solid Films*, 232, 56 (1993).
19. M. Ritala, M. Leskellä, L. Niinistö, and E. Rauhala, *Chem. Mater.*, 5, 1174 (1993).
20. C. S. Kang, C. S. Hwang, H.-J. Cho, B. T. Lee, S. O. Park, J. W. Kim, H. Horii, S. I. Lee, Y. B. Koh, and M. Y. Lee, *Jpn. J. Appl. Phys.*, 35, 4390 (1996).
21. H. Yamaguchi, P.-Y. Lesnicherre, T. Sakuma, Y. Miyasaka, A. Ishitani, and M. Yoshida, *Jpn. J. Appl. Phys.*, 32, 4069 (1993).
22. Joint Committee on Powder Diffraction Standards, Card 35-734, JCPDS, International Center for Diffraction Data, Newtown Square, PA.
23. G. W. Dietz, W. Anpöhler, M. Klee, and R. Waser, *J. Appl. Phys.*, 78, 6113 (1995).
24. Y. Park, V. Choong, Y. Gao, B. R. Hsieh, and C. W. Tang, *Appl. Phys. Lett.*, 68, 2699 (1996).
25. T. Chiba, K. Itoh, and O. Matsumoto, *Thin Solid Films*, 300, 6 (1997).
26. J. Zeng, H. Wang, M. Wang, S. Shang, Z. Wang, and C. Lin, *Thin Solid Films*, 322, 104 (1998).
27. T. W. Kim, M. Jung, H. J. Kim, Y. S. Soon, W. N. Kang, and S. S. Yom, *Appl. Phys. Lett.*, 62, 1788 (1993).
28. T. W. Kim and S. S. Yom, *Appl. Phys. Lett.*, 65, 1955 (1994).
29. Y. S. Yoon, D. H. Lee, T. S. Kim, M. H. Oh, and S. S. Yom, *J. Vac. Sci. Technol. A*, 12, 751 (1994).

# Digital chemical vapor deposition of $\text{SiO}_2$

M. Nakano, H. Sakaue, H. Kawamoto, A. Nagata, M. Hirose,  
and Y. Horiike

*Department of Electrical Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan*

(Received 9 March 1990; accepted for publication 22 June 1990)

The repetitive cycles of a few monolayers hydrogenated silicon deposition and its oxidation has been employed for the growth of  $\text{SiO}_2$ . The surface reaction is promoted by an alternate irradiation of silicon hydride radical beam produced by the upstream pulsed microwave discharge of  $\text{SiH}_4$  and discharged oxygen beam. The deposition rate is controlled by the flow velocity of silane gas jet and substrate temperature. It is shown that the deposition species ejected with supersonic velocity into a high vacuum reactor conformably fills the  $\text{SiO}_2$  film into a deep Si trench.

Continuous shrinkage of device size in very large scale integrated (VLSI) circuits has led to the necessity for the vertical integration of circuit elements as in the case of Si trench capacitors, three-dimensional stacked capacitors, and multilevel metallization. This requires a high aspect ratio (depth/linewidth) structure and subsequent filling of the structure with insulator or conductor. Plasma-enhanced chemical vapor deposition (PECVD) has been widely used as a filling technology. However, the gas phase precursors in a plasma generally degrade the step coverage to cause harmful voids in deep trenches and via holes. In order to avoid such degradation and to perform the conformable CVD, it is of crucial importance to suppress the gas phase reactions and in turn to enhance the surface dominant reaction.

To meet these requirements, a layer-by-layer deposition technique similar to atomic layer epitaxy (ALE) and molecular layer epitaxy (MLE), which are new growth methods for II-VI and III-V compound semiconductors,<sup>1-3</sup> has to be developed as a novel CVD. In ALE and MLE systems, a self-limiting surface reaction induced by metal-organic compounds controls the growth rate. However, such a self-limiting process of surface reaction is not involved in CVD of insulators such as  $\text{SiO}_2$ . Layer-by-layer CVD of insulators could be realized by a precise monolayer control in supplying deposition species. This letter reports a novel CVD method of  $\text{SiO}_2$ . The repetitive cycles of silicon hydride radical adsorption and its subsequent oxidation with oxygen radical beam results in layer-by-layer growth of oxide. We call this technique pulsed or digital CVD.

The concept of a digital CVD reactor is schematically shown in Fig. 1. Monosilane diluted to 18.5% He and pure oxygen were alternately supplied into the microwave (2.45 GHz) discharge portions by using piezovalves. Silicon hydride and oxygen radicals generated from remote microwave-discharged plasmas<sup>4</sup> were alternately irradiated onto a Si wafer surface in the reactor through a sloped nozzle tube and a straight (13 mm $\phi$ ) quartz tube. The distances between these tube edges and the wafer surface are 40 mm. In order to moderate the drop of  $\text{SiH}_4$  gas temperature due to an adiabatic expansion and also to reduce the velocity of the gas jet, a buffer tube equipped with

fins was connected to the outlet of the piezovalve. The wafer temperature can be controlled in the range from  $-20$  to  $500^\circ\text{C}$ . Flow pulse width for  $\text{SiH}_4$  was fixed at 50 ms and flow pulse widths for  $\text{O}_2$  were changed from 1 to 10 s. The interval between both gas flows was held at 1 s. During the whole deposition sequence the reactor was continuously evacuated by a turbomolecular pump.

First,  $\text{SiH}_4$  gas was injected without discharge to grow a thin film. However, no film growth was observed in the temperature range from  $-20$  to  $500^\circ\text{C}$ . Next,  $\text{SiH}_x$  radicals with high sticking probability<sup>5</sup> were generated by microwave discharge using a coaxial waveguide, and an oxide film was successfully formed at room temperature. It was found that without using the buffer, a supercooled  $\text{SiH}_x$  radical was deposited on an extremely small area on the wafer with a high deposition rate of 100 Å/pulse at room temperature. Consequently, the buffer shown in Fig. 1 was added. As the buffer temperature is increased, the film thickness was decreased, while the deposition area becomes larger. The deposition rate was also decreased monotonically with increasing substrate temperature. These decreases probably result from a lowering of sticking probability of the  $\text{SiH}_x$  radicals. Figure 2 shows the  $\text{SiO}_2$  film thickness as a function of the number of injected pulses for a room-temperature wafer or  $300^\circ\text{C}$  wafer with a buffer temperature of  $300^\circ\text{C}$ . The deposition rate of  $\text{SiO}_2$  on a wafer area of  $1\text{ cm}^2$  was 3 Å/pulse under the conditions of pulse widths of 50 ms for  $\text{SiH}_4$  and 5 s for  $\text{O}_2$  and at a wafer temperature of  $300^\circ\text{C}$ . The deposition rate was defined by dividing the maximum film thickness by the number of pulses.

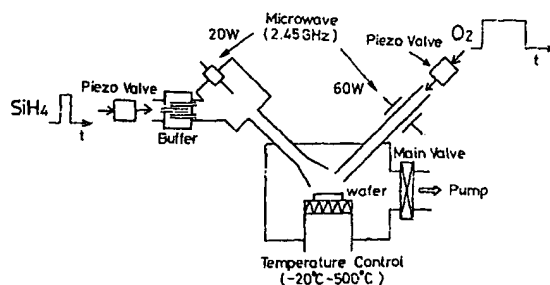


FIG. 1. Schematic illustration of a digital CVD apparatus.

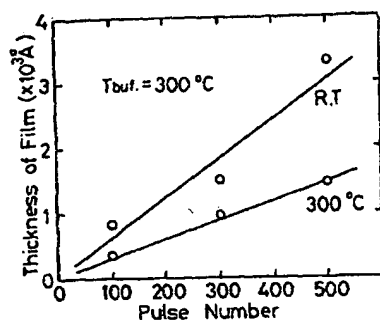


FIG. 2.  $\text{SiO}_2$  film thickness as a function of number of pulses for wafer temperatures of RT and  $300^\circ\text{C}$  at the buffer temperature  $T_{\text{buf}} = 300^\circ\text{C}$ .

The ratio of integrated infrared absorption intensity for Si—OH and Si—O bonds obtained from Fourier transform infrared (FT-IR) spectroscopy measurements as a function of  $\text{O}_2$  pulse width at a fixed buffer temperature of  $300^\circ\text{C}$  is shown in Fig. 3. The origin of a large amount of Si—OH bonds at a low substrate temperature and at a shorter  $\text{O}_2$  pulse width is interpreted in term of the formation of a polysilane-like film structure,<sup>6</sup> which is not efficiently oxidized. It is evident that the amount of Si—OH bonds was significantly decreased with increasing the irradiation time of oxygen radicals. This demonstrates an advantage of digital CVD because the film quality is improved by independent control of deposition parameters. Although the stoichiometry of grown oxide was confirmed by the ellipsometry, the film etch rate by buffered hydrofluoric acid (BHF) was considerably faster than that of thermal  $\text{SiO}_2$ .

During the course of this study,  $\text{SiH}_x$  radicals impinging obliquely on a wafer were found to be reflected from the surface. Nevertheless, the film deposition occurred on the shadowed region of the injected radial beam. As shown in Fig. 4, the oxide deposition rate on the top surface decreases as the  $\text{SiH}_x$  radical incidence angle increases for 700 cycles of deposition. The cosine dependence of depo-

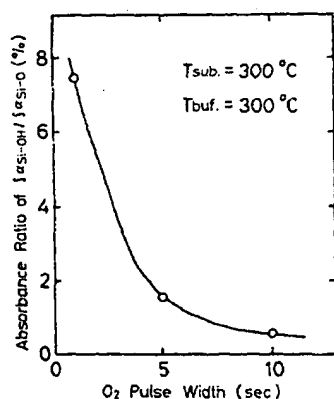


FIG. 3. Integrated infrared absorption intensity of Si—OH to Si—O bonds as a function of pulse width of  $\text{O}_2$  gas at the buffer temperature  $T_{\text{buf}} = 300^\circ\text{C}$  and the wafer temperature  $T_{\text{sub}} = 300^\circ\text{C}$ .

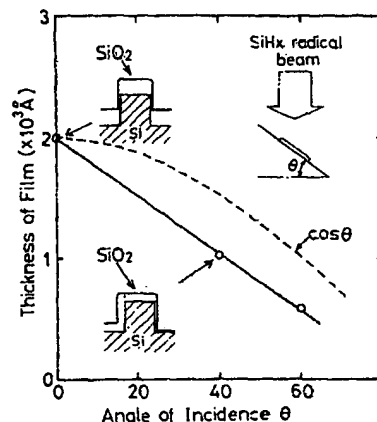


FIG. 4. Film thickness was obtained from the scanning electron microscopy (SEM) micrograph in which the value of the top surface thickness was measured. The sidewall thickness in the inset is only schematic.

sition rate is also shown in the figure when it is assumed that the deposition rate is determined by the flux intensity of  $\text{SiH}_x$  radical beam and that the beam reflection at normal incidence is negligible. The deviation of the actual deposition rate on the top surface from the calculated curve is ascribable to the reflected rate of incident  $\text{SiH}_x$  beam. It is also suggested from this result that although the flow velocity of  $\text{SiH}_4$  gas is considerably decelerated by the use of the buffer, the neutral  $\text{SiH}_x$  beam still has near supersonic velocity.

The oxide filling into Si trenches by utilizing a configuration of the obliquely incident  $\text{SiH}_x$  beam was difficult, while normal incidence of the  $\text{SiH}_x$  beam showed satisfactory filling of  $\text{SiO}_2$  into trenches with an aspect ratio of 2 for  $1.5\text{ }\mu\text{m}$  L&S as shown in Fig. 5. The observation of the oxide-filling process demonstrates that the  $\text{SiO}_2$  film grows a little faster on the bottom rather than on the sidewall of the trench. This might arise from the fact that  $\text{SiH}_x$  radicals with normal incidence stick more on both the upper and bottom surfaces of the trench because the radical beam is significantly reflected on the sidewall. At the present stage,  $\text{SiO}_2$  could not be filled in trenches with aspect ratios larger than 3. In conventional plasma CVD employing a  $\text{SiH}_4 + \text{O}_2$  mixture, the trench filling has not been achieved

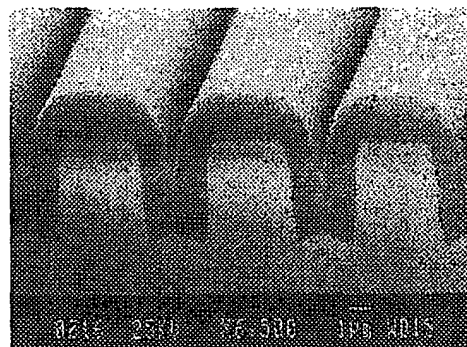


FIG. 5. Cross-sectional SEM photograph of Si trenches filled with  $\text{SiO}_2$ .

even by an aspect ratio of 1. For the primary aim of completely conformable digital CVD, the film deposition mode totally controlled by surface reactions must be developed by decelerating the injected  $\text{SiH}_x$  radical velocity.

In conclusion, digital CVD which is done by repeating one cycle consisting of deposition of remote microwave-discharged silicon hydride radicals and its subsequent oxidation has been developed for growing  $\text{SiO}_2$  films. The deposition rate of 3 Å/pulse is achieved by controlling the flow velocity of the  $\text{SiH}_4$  gas jet and the pulse width of the  $\text{O}_2$  radicals. The deposition species ejected with supersonic velocity into a high vacuum reactor fills a  $\text{SiO}_2$  film into a trench successfully.

- <sup>1</sup>T. Suntola, *Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984* (Business Center for Academic Societies Japan, Tokyo, 1984), p. 647.
- <sup>2</sup>J. Nishizawa, H. Abe, and T. Kurabayashi, *J. Electrochem. Soc.* **132**, 1197 (1985).
- <sup>3</sup>A. Doi, Y. Aoyagi, and S. Mamba, *Materials Research Society Symposium Proceedings (Photon, Beam, and Plasma Stimulated Chemical Processing at Surface), No. 75, Boston 1986* (Materials Research Society, Pittsburgh, 1986), p. 217.
- <sup>4</sup>M. Shibagaki, Y. Horiike, and T. Yamazaki, *Jpn. J. Appl. Phys.* **17**, 215 (1978).
- <sup>5</sup>S. Miyazaki, H. Hirata, and M. Hirose, *Extended Abstracts of 16th (1984 International) Conference on Solid State Devices and Materials Kobe, 1984* (Business Center for Academic Societies Japan, Tokyo, 1984), p. 447.
- <sup>6</sup>M. H. Brodsky, M. Cardona, and J. J. Cuomo, *Phys. Rev. B* **16**, 3556 (1977).